STARCH MODIFICATION OF THE FLOCCULATION
AND FLOTATION OF APATITE

by

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Although the technical literature contains abundant references on applications of starch in mineral processing, the majority is not concerned with phosphate mineral systems. Nevertheless, the interaction between starch and apatite surfaces is relevant to both selective flocculation and flotation of phosphate ores. The main objective of this thesis is to investigate in detail such interaction in order to provide a more clear understanding on the behaviour of apatite/starch systems.

Considerable research effort was dedicated to a thorough characterization of the starch samples used, especially in those aspects most pertinent to the application of starches as flocculants and depressants. Presence of ionic impurities in the starch samples tested was identified by infrared spectroscopy and microelectrophoresis. These impurities (proteins, carboxylic groups and, possibly, phosphate esters) were found to play an important role in the mechanisms governing the interaction of starch macromolecules and mineral surfaces.

In a first stage of this research, the interaction between aqueous solutions of starches (and starch fractions - amylose and amylopectin) with calcium ionic species and surfactants (flotation collectors) was investigated.
Depression of solution electrical conductivity, experienced in Ca-starch systems, was indicative of chemical reactions taking place (complexation). For surfactants, evidence for their interaction with starch fractions was obtained by UV-Vis. spectroscopy. The spectra of starch/surfactant solutions in the presence of iodine were altered indicating the substitution of iodine species by surfactant molecules at the helical sites of starch macromolecules.

The next step involved the study of the adsorption of starch onto both apatite and silica mineral surfaces. Preliminary tests pointed out that a much stronger interaction took place in the case of apatite. Starch adsorption isotherms obtained for fluorapatite and quartz confirmed the preferential adsorption of starch onto the phosphate mineral surface. Both amylose and amylopectin were strongly adsorbed on fluorapatite but the latter polymer displayed the largest extent of interaction on a weight per area basis. The shape of the adsorption isotherms for the two starch fractions on fluorapatite also corroborates the idea of a stronger interaction by amylopectin. In turn, whole starches displayed adsorption isotherms resembling more closely that obtained for amylopectin.

Adsorption of starches on fluorapatite was increased considerably in the presence of Ca ionic species.
In the absence of externally added Ca ionic species, the amount of Ca released by the mineral surface was dependent upon the amount of starch adsorbed. These two phenomena can be interpreted as indicating the importance of Ca sites and presence of Ca species for the adsorption of starches, hence justifying the preferential adsorption displayed for apatite. Adsorption of starch on quartz surfaces was also enhanced in the presence of Ca ionic species, once more confirming the important role played by calcium on the adsorption of starches.

Flocculation studies were also conducted with fluorapatite, kaolinite and quartz suspensions in the presence of different starches. Under the conditions tested, all starches samples failed to promote aggregation of the two non Ca-bearing minerals. In turn, fluorapatite suspensions were flocculated rather strongly by all starches. Maximum flocculation of fluorapatite was achieved at partial polymer coverage conditions. With one exception (amylose), increasing the concentration of the polymers above an optimum level, generated partial re-stabilization of the suspensions, probably via a steric effect.

All starches depressed both anionic and cationic flotation of fluorapatite. Amylose was the least effective depressant among all starches, especially for the cationic
flotation system. The depressant action was a function of pH and of the relative amounts of polymer and surfactant. Alkaline pH favoured depression, whereas as the collector level was increased, the depressant action was diminished and eventually eliminated.

The experimental evidence gathered in the present research supports a chemical mechanism for the interaction between starch and apatite surfaces. Calcium plays a dominant role, and its importance for the adsorption of starches onto mineral surfaces is most probably related to the formation of complexes between starch impurity-related ionic groups and Ca ionic species. Hydrogen bonding and to lesser extent electrostatic forces are also important for the overall interaction between starch and apatite surfaces. The larger extent of interaction for the amylopectin fraction (highest molecular wt.) as compared to that of amylose (lowest molecular wt. fraction) gives support for the accessory role of hydrogen bonding.
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ACKNOWLEDGMENTS

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Technical assistance was provided by a number of people at various stages of this research. For their considerable help, especially to Mrs. S. Finora and Mr. F. Schmidiger, my sincere thanks.

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Help in all aspects was constantly provided by my wife Mary. Without her support, understanding and caring, this work would never have been finished. To Mary I dedicate this thesis and express my most deep gratitude.

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CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico, Brazil) and also by the William A. MacKenzie Scholarship and Cy and Emerald Keyes Fellowship. The author is deeply indebted to his sponsors and also to the Universidade Federal de Minas Gerais for the concession of a leave of absence.
Starches are extensively used in the processing of many ores. They can act as depressants in both anionic and cationic flotation circuits. In the past they have also been used as flocculants for fine tailings, and today they are still used as selective flocculants in the selective flocculation-flotation of low grade iron ores.

Flotation of phosphate ores is a relatively well established practice. Although this process has been in use for more than 40 years, many problems are still encountered. Among them, high losses to fines, poor selectivity for calcitic and/or dolomitic ores and low enrichment ratios are most frequent.

In the flotation of some phosphate ores, starches act as depressants of calcite and dolomite in the anionic flotation of apatite. They have been tested as selective flocculants for phosphate fines in many instances. One of the first attempts in the field of selective flocculation was related to the beneficiation of phosphate fines discarded in the processing of sedimentary phosphate ores from Florida, USA. Vast amounts of relatively rich phosphatic "slimes" are lost in the beneficiation of these ores. Haseman (1953) patented a process to increase the overall recovery by selectively flocculating these slimes with starch. Although the results were encouraging, due to some technical difficulties allied to economic considerations, the studies
were not further pursued. Since then, several other attempts were made in this field. They will be discussed later on in this thesis.

The literature review section of this thesis gives an overall picture of the phosphate mineral industry, the state-of-the-art of the beneficiation of phosphate ores and the chemistry and physico-chemistry of starches and their applications in mineral processing.
2 - OBJECTIVE

The objective of this thesis is to investigate the fundamental aspects of the flotation and flocculation of apatite in the presence of different starches. To achieve this objective the following research was conducted:

(i) - characterization of the starch samples used: their composition and aqueous solution chemistry.
(ii) - study of the adsorption behaviour of starches onto apatite surfaces.
(iii) - study of flocculation of apatite with starches.
(iv) - study of the depressant action of starches in the flotation of apatite with sodium oleate and dodecylamine hydrochloride.
3 - SCOPE AND IMPORTANCE OF THE PRESENT WORK

The scope of this thesis is to investigate in detail the fundamental aspects of the interaction between starch and apatite surfaces, as applied to the flotation and flocculation of this mineral. The model system chosen includes pure mineral samples of apatite and different starches (reagent and commercial grade). Many other chemicals were utilized, including pH modifiers, salts of commonly occurring ions such as calcium and magnesium, and different dispersants (other than pH modification). The selection of these reagents was based on published information on this subject (current practice and research papers), and also on some preliminary testwork.

Although previous research work on similar systems is available in the literature, fundamental studies such as the adsorption behaviour of starches onto apatite surfaces are very scanty. In contrast for example, the industrial application of the selective flocculation process for the treatment of low grade iron ores was pre-dated by many studies of fundamental character (Iwasaki, 1965, Iwasaki and co-workers, 1969; Balajee and Iwasaki 1969; just to cite a few). One of the main contributions of the present work is to fill this void in the field of the beneficiation of phosphate ores.
This work also aims to provide a more complete understanding of the mechanisms prevailing in the interaction between starches and apatites. For instance, the role of calcium aqueous ionic species in both adsorption and flocculation of apatite with starch was found to be very important. The very high affinity of starch for the apatite surface is probably a direct consequence of the presence of Ca sites at the interface. The importance of Ca in the adsorption of starches on apatite suggests that monitoring its concentration in flotation and flocculation systems involving apatite and other Ca bearing minerals is, at least, strongly advised.
4 - REVIEW OF THE LITERATURE

4.1 - Phosphate Minerals, Rock and Ores


The term "phosphate rock" (or "commercial phosphate rock"), as normally used in the phosphate industry, refers to a sedimentary phosphatic material, concentrated or only washed and classified, containing a minimum saleable grade. In some cases, phosphate rock has a more general meaning, being used to describe any phosphate product that is traded in the market, irrespective of the origin of the material. In this report phosphate rock(*) will be used in its more general sense, describing either a treated ore (an igneous or a sedimentary phosphate concentrate) or a classified, washed and/or calcined high grade ore.

Apatite is also a term used in the industry to describe the phosphate concentrate produced from an igneous ore. Due to the adopted meaning of phosphate rock, apatite will not be used here in this meaning. Wherever apatite is referred to it will have only its mineralogical meaning.

(*) Phosphorite is the geological term used to describe a sedimentary phosphate rock. Although most phosphate ores mined today are phosphorites, a phosphorite is essentially a geological term, without any relationship to the exploitability of the rock as a phosphate ore.
A phosphate ore is defined for the purpose of this report as any rock (sedimentary, metamorphic or igneous) containing enough phosphorus to make it an economically exploitable source of phosphate.

Phosphorus pentoxide (%P₂O₅) is one of the conventional ways to express value content in the phosphate industry. Also very common are %B.P.L. The conversion figures are as follows:

\[
\%P_{2}O_{5} = 0.4576\% \text{ B.P.L. or } \%T.P.L.
\]

\[
\%P_{2}O_{5} = 2.2915\% P
\]

Marketable phosphate rock entering international trade usually contains more than 30% P₂O₅ (65% B.P.L.). Some restrictions concerning other elements apply. For example, the so called "R₂O₃ grade" (Al₂O₃ + Fe₂O₃) may not exceed 3 - 5% in most cases, and a chloride content greater than 600 ppm can cause serious corrosion problems. Lower grade phosphate rock (approx. 24 - 26% P₂O₅) is used in some cases for direct application to impoverished soils. Details on the different specifications for phosphate rock are given by Lehr and McClellan, 1973 and Gremillion and McClellan, 1975.
4.1.2 - Production and Reserves

Table 4.I shows the world phosphate rock production by country for the period from 1980 to 1984. In the same table measured reserves of phosphate ores are also included. Data for the 1984 fertilizer year were recently published by Weston (1985). They show an increase of approximately 6.5% over the 1983 figure (143 million tonnes in 1984 compared to 134 million tonnes in 1983). World production is expected to double by the year 2000 (Lawver et al., 1978). Such a dramatic increase reflects the need to increase agricultural yields through the use of fertilizers. Discussion on the production and demand trends and more detailed information on this subject, can be found on the literature (see for example: Emigh, 1978 and 1983; Barry, 1980; Stowasser, 1980; Manderson, 1978; Anonymous, 1981).

World reserves shown in Table 4.I represent only exploitable material that is reasonably well known. The principal reserves are in Morocco and the U.S.S.R. (approximately 54% and 13% of the world total, respectively).

Relatively well known resources (presently uneconomic deposits, due to either current prices or lack of technology) of phosphate rock, amount to the order of at least 200-300 billion tonnes (Notholt and Hartley, 1983). Emigh (1972) estimated the potential resources of phosphate at 1,177,000 million tonnes.
<table>
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<tr>
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<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
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<tr>
<td></td>
<td>1,000 tonnes</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>North America</td>
<td>54,745</td>
<td>53,745</td>
<td>37,829</td>
<td>41,890</td>
<td>48,820</td>
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<td>53,624</td>
<td>37,414</td>
<td>41,890</td>
<td>48,820</td>
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<td>Mexico</td>
<td>330</td>
<td>252</td>
<td>415</td>
<td>-</td>
<td>-</td>
<td>500,000</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>2,300,000</td>
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<tr>
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<td>2,732</td>
<td>3,208</td>
<td>3,400</td>
<td>2,500,000</td>
</tr>
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<td>15</td>
<td>18</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Peru</td>
<td>14</td>
<td>12</td>
<td>29</td>
<td>-</td>
<td>-</td>
<td></td>
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<tr>
<td><strong>TOTAL</strong></td>
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<td></td>
<td></td>
<td></td>
<td>2,500,000</td>
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<td>25,549</td>
<td>26,963</td>
<td>27,700</td>
<td>28,890</td>
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<td>Eastern Eur.) and U.S.S.R.)</td>
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<td>25,220</td>
<td>26,600</td>
<td>27,700</td>
<td>28,890</td>
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<tr>
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<td>363</td>
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<tr>
<td><strong>TOTAL</strong></td>
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<td></td>
<td></td>
<td></td>
<td>4,515,000</td>
</tr>
<tr>
<td>Africa</td>
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<td>33,200</td>
<td>29,906</td>
<td>32,103</td>
<td>33,622</td>
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<td>19,696</td>
<td>17,753</td>
<td>20,106</td>
<td>21,133</td>
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<td>Senegal</td>
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<td>1,927</td>
<td>975</td>
<td>1,250</td>
<td>1,874</td>
<td>130,000</td>
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<tr>
<td>South Africa</td>
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<td>3,034</td>
<td>3,173</td>
<td>2,742</td>
<td>2,593</td>
<td>3,000,000</td>
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<td>Tunisia</td>
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<td>4,596</td>
<td>4,196</td>
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<td>5,346</td>
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<td>3,809</td>
<td>2,081</td>
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<td>3,100,000</td>
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<td></td>
<td></td>
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<td>4,515,000</td>
</tr>
<tr>
<td>Asia</td>
<td>20,247</td>
<td>20,910</td>
<td>23,038</td>
<td>22,646</td>
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<td>Israel</td>
<td>2,611</td>
<td>2,373</td>
<td>2,711</td>
<td>2,969</td>
<td>3,312</td>
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<tr>
<td>Jordan</td>
<td>4,243</td>
<td>4,244</td>
<td>4,431</td>
<td>4,749</td>
<td>6,263</td>
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<td>China</td>
<td>10,726</td>
<td>11,500</td>
<td>12,500</td>
<td>12,500</td>
<td>13,200</td>
<td>1,000,000</td>
</tr>
<tr>
<td>Syria</td>
<td>1,319</td>
<td>1,321</td>
<td>1,455</td>
<td>1,229</td>
<td>1,514</td>
<td>200,000</td>
</tr>
<tr>
<td>Vietnam</td>
<td>400</td>
<td>500</td>
<td>500</td>
<td>-</td>
<td>-</td>
<td>100,000</td>
</tr>
<tr>
<td>Other</td>
<td>948</td>
<td>972</td>
<td>1,441</td>
<td>1,199</td>
<td>850</td>
<td>100,000</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1,600,000</td>
</tr>
<tr>
<td>Oceania</td>
<td>3,800</td>
<td>2,918</td>
<td>2,922</td>
<td>2,779</td>
<td>2,611</td>
<td></td>
</tr>
<tr>
<td>Australia/Christmas Is.</td>
<td>1,713</td>
<td>1,438</td>
<td>1,563</td>
<td>1,095</td>
<td>1,252</td>
<td>100,000</td>
</tr>
<tr>
<td>Nauru</td>
<td>2,087</td>
<td>1,480</td>
<td>1,359</td>
<td>1,684</td>
<td>1,359</td>
<td></td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Not Specified</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3,995</td>
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<tr>
<td><strong>WORLD TOTAL</strong></td>
<td>139,501</td>
<td>139,244</td>
<td>123,437</td>
<td>134,321</td>
<td>142,977</td>
<td>34,445,000</td>
</tr>
</tbody>
</table>

(*) Data in this table are from:

(**) Preliminary.
At present rates of increase, known reserves should last for at least 200 years.

4.1.3 - Uses

More than 90% of world phosphate rock is utilized for agricultural purposes, mainly in the manufacture of phosphatic fertilizers (Notholt and Hartley, 1983). Low-grade "straight" phosphatic fertilizers, such as superphosphate are now being superceded by highly concentrated, multi-nutrient (NPK) formulations, based on ammonium phosphate and triple superphosphate. These high-grade fertilizers now account for more than one-half of world consumption of phosphate rock. Details of the production of phosphoric acid (intermediate product) and NPK fertilizers can be found in the literature (de Lima, 1976; McLellan, 1983; Anonymous, 1981).

Other uses include the manufacture of animal feed supplements, direct application to acidic soils, detergents, soaps, fire retardants, elemental phosphorus, insecticides, and pharmaceutical chemicals (de Lima, 1976 and Notholt and Hartley, 1983).
4.1.4 - Mineralogy and Geology

Although there are at least 350 recognized phosphate minerals (Nriagu, 1984), very few of them are important in terms of phosphate ores. Actually only those in the apatite series can be regarded as ore minerals for phosphate.

Table 4.II presents a summary of some properties of members of the apatite series. Table 4.III gives a compilation of chemical analyses of various apatites, some of which are present in the phosphate ores. There is no simple way to represent these minerals by a unique chemical formula. For apatites of igneous or metamorphic origin, one possible generalized formula is as follows:

\[ \text{Me}_{10}(\text{XO}_4)_6\text{Z}_2 \]

where  
- \( \text{Me} = \text{Ca, Sr, Ba, Mn, Y} \)
- \( \text{X} = \text{P (mainly)} \)
- \( \text{Z} = \text{OH, F, Cl, Br} \).

Sedimentary apatites are much more complex and the degree of substitution of lattice ions is much higher. Nathan (1984) gives some of the possibilities (see table 4.IV). The existence of so many substitutions is related to the type of lattice of apatite. An "open lattice", allows
TABLE 4.II - Some Examples of Minerals in the Apatite Series (from Nriagu, 1984)(*)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Density</th>
<th>Strongest Diffraction Lines</th>
<th>Discredited Names</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorapatite</td>
<td>Ca$_{10}$(PO$_4$)$_6$F$_2$</td>
<td>3.1-3.2</td>
<td>2.800(100), 2.702(60)</td>
<td>-</td>
</tr>
<tr>
<td>Chlorapatite</td>
<td>Ca$_{10}$(PO$_4$)$_6$Cl$_2$</td>
<td>3.1-3.2</td>
<td>2.78(100), 2.86(55)</td>
<td>-</td>
</tr>
<tr>
<td>Hydroxyapatite</td>
<td>Ca$_{10}$(PO$_4$)$_6$(OH)$_2$</td>
<td>3.08</td>
<td>2.814(100), 2.778(60)</td>
<td>-</td>
</tr>
<tr>
<td>Strontium-apatite (Sr,Ca)$_{10}$(PO$_4$)$_6$(OH,F)$_2$</td>
<td>3.84</td>
<td>2.89(100), 3.167(70)</td>
<td>Saamite</td>
<td></td>
</tr>
<tr>
<td>Carbonate-apatite Ca$_5$(PO$_4$,CO$_3$)$_3$(OH,F)(**)</td>
<td>2.9-3.1</td>
<td>2.822(100), 2.722(90)</td>
<td>Collophane, Monite; Naurite, Kurskite, Grodnolite</td>
<td></td>
</tr>
<tr>
<td>Wilkeite</td>
<td>Ca$_5$(SiO$_4$,PO$_4$,SO$_4$)$_3$(OH,F)</td>
<td>3.12</td>
<td>2.80(100), 2.70(90)</td>
<td>-</td>
</tr>
</tbody>
</table>

(*) Most minerals in this series belong to the Hexagonal System, class 6/m.

(**) At least two well defined varieties are known:
Francolite (Ca$_3$F)$_2$(P,C)$_6$(O,OH,F)$_2$4(Ca,C)$_4$, and
Dahllite Ca$_6$(OH)$_2$(P,C)$_6$O$_2$4(Ca,C)$_4$
TABLE IV. III - Chemical Analyses of Apatites (*) (major elements only)

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>P_2O_5</td>
<td>42.2</td>
<td>41.3</td>
<td>40.98</td>
<td>42.19</td>
<td>42.20</td>
<td>36.3</td>
<td>37.1</td>
<td>40.1</td>
<td>34.7</td>
<td>38.2</td>
</tr>
<tr>
<td>CaO</td>
<td>55.6</td>
<td>55.16</td>
<td>52.40</td>
<td>55.47</td>
<td>50.0</td>
<td>55.4</td>
<td>55.5</td>
<td>55.6</td>
<td>55.2</td>
<td>54.7</td>
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<tr>
<td>F</td>
<td>3.77</td>
<td>3.67</td>
<td>1.15</td>
<td>1.01</td>
<td>3.5</td>
<td>4.68</td>
<td>4.56</td>
<td>4.09</td>
<td>4.93</td>
<td>2.8</td>
</tr>
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<td>0.09</td>
<td>3.74</td>
<td>-</td>
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<td>-</td>
<td>-</td>
<td>n.a</td>
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</tr>
<tr>
<td>H_2O</td>
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<td>0.06</td>
<td>1.73</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<td>CO_2</td>
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<td>-</td>
<td>4.53</td>
<td>3.95</td>
<td>1.59</td>
<td>5.70</td>
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<td>1.41</td>
<td>2.27</td>
<td>0.66</td>
<td>4.40</td>
<td>1.28</td>
<td>1.08</td>
<td>0.39</td>
<td>1.80</td>
<td>0.1</td>
</tr>
</tbody>
</table>

(*) references for this table are: Palache et al., 1951; McClellan and Clayton, 1982; Nriagu, 1984.

1 - Theoretical fluorapatite
2 - Fluorapatite, Ontario, Canada
3 - Chlorlan fluorapatite, Kurohura, Japan
4 - Fluorian hydroxylapatite, Hospenthal, Switzerland
5 - Fluorapatite, Jacupiranga, Brazil
6 - Francolite, Morocco
7 - Francolite, Florida, U.S.A.
8 - Francolite, Western U.S.A.
9 - Francolite, Tunisia
10 - Fluorapatite, Durango, Mexico
different ionic species to replace one or all of the original components of pure (end) members of the apatite series. Carbonate-apatite (i.e. apatite containing Co$_3$ ions partially substituting for PO$_3^-$ ions) is the most common type of apatite found in sedimentary deposits. Francolite (or carbonate-fluorapatite) probably has the chemical composition most nearly typical of apatites utilized as sources of phosphorus. McClellan and Clayton (1982) proposed a model for francolite, incorporating the hydroxyl variety, as follows:

\[ \text{Ca}_{10-x-y}\text{Na}_x\text{Mg}_y(\text{PO}_4)_{6-z}(\text{CO}_3)_z\text{F}_{0.4z}(\text{F,OH})_2 \]

with \( y = 0.4x \) and \( x/(6-z) = 0.30 \).

This model emphasizes the complexity of the chemical composition of different apatites. This complexity points to the need for site specificity of mineral processing studies with phosphate ores. Although some properties might not change significantly with the origin of, and substituents in the apatites, surface properties can be dominated even by small chemical changes.
TABLE 4.IV - Some Possible Substitutions in the Apatite Structure (after Nathan, 1984).

<table>
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<tr>
<th>Constituent ion</th>
<th>Substituting ion</th>
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<td>Ca$^{2+}$</td>
<td>Na$^+$, K$^+$, Ag$^+$</td>
</tr>
<tr>
<td></td>
<td>Sr$^{2+}$, Mg$^{2+}$, Mn$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, Ba$^{2+}$</td>
</tr>
<tr>
<td></td>
<td>Sc$^{3+}$, Y$^{3+}$, R.E. $^{3+}$, Bi$^{3+}$</td>
</tr>
<tr>
<td></td>
<td>U$^{4+}$</td>
</tr>
<tr>
<td>PO$_4^{3-}$</td>
<td>CO$_3^{2-}$, SO$_4^{2-}$, CrO$_4^{2-}$</td>
</tr>
<tr>
<td></td>
<td>AsO$_4^{3-}$, VO$_4^{3-}$, CO$_3$.F$^{3-}$, CO$_3$.OH$^{3-}$</td>
</tr>
<tr>
<td></td>
<td>SiO$_4^{4-}$</td>
</tr>
<tr>
<td>F$^-$</td>
<td>OH$^-$, Cl$^-$, Br$^-$</td>
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<tr>
<td></td>
<td>O$^{2-}$</td>
</tr>
</tbody>
</table>
Today's phosphate ores are basically of two types: igneous and sedimentary. Sedimentary phosphates (mostly phosphorites) are the most important, accounting for more than 82% of the world production and over 95% of the known resources and reserves (Cook, 1984).

In the case of igneous deposits there are again two major types: primary and secondary (or residual). Primary deposits are normally related to alkaline and carbonatitic intrusions (plutons). They generally have small areas (1 to 50 km²). These rocks are characterized by their high degree of crystallinity. In terms of mineralogy, the phosphate mineral is usually apatite (predominantly fluorapatite). Non-phosphatic minerals include silicates such as feldspars and pyroxenes for alkaline intrusions (e.g. Kola Peninsula complex, U.S.S.R.), and calcite and dolomite for carbonatitic deposits (e.g. Jacupiranga, Brazil). Residual (secondary) igneous deposits are formed by the weathering of the original carbonatitic intrusions. Many deposits exploited today belong to this type (e.g., Catalao, Araxá, Tapira and Ipanema in Brazil; Sukulu and Tororo in Uganda; Lueshe in Zaire). Several residual carbonatitic deposits are known in Ontario, Canada, such as Cargill (19.6% P₂O₅, estimated 56.7 million tonnes), Martison Lake, Schryburt Lake and Goldray (Anon., 1981). Details on the world carbonatites can be found in Tuttle and Gittins, 1966. Emigh (1983) also describes some of the igneous deposits utilized as sources of phosphate.
Sedimentary phosphate deposits are known to occur on every continent except Antarctica (Cook, 1976). Their ages range from the Precambrian to Recent. They can be classified as follows:

(i) Geosynclinal
(ii) Platform
(iii) Weathered or Residual.

In the first category, two types are distinguished: eugeosynclinal and miogeosynclinal. In economic terms only miogeosynclinal deposits are important. Some examples are the Karatau deposits in the U.S.S.R. and the Western Phosphate Field of the U.S.A. (Phosphoria Formation). These deposits are characterized by a common association with chert, fine organic rich argillaceous sediments, and carbonates (particularly dolomite). These phosphorites tend to be pelletal and commonly extend over hundreds to thousands of square kilometres. $P_2O_5$ content is high throughout.

Platform phosphorites are generally found on, or bordering cratons. Deposits occur as rich discrete pockets tens to hundreds of square kilometres in area, and several metres thick. Examples are the Pamlico Sound deposit of North Carolina, U.S.A. and the Mishash deposits of Israel. Alternatively they occur as thin low-grade nodular deposits of the Moscow basin of U.S.S.R. They are commonly associated with terrigenous sediments such as quartz siltstone and sandstone or with carbonates. Glauconite is abundant in some
deposits.

Weathered phosphorites are typified by the Pliocene Bone Valley Formation of Florida, U.S.A. Concentration of phosphate can occur as a result of chemical or mechanical weathering, the first being responsible for producing a high-grade phosphorite by the leaching-out of a more soluble (generally calcareous) nonphosphatic matrix. Reworked deposits such as the Bone Valley phosphorite are commonly "pebbly" and nodular. Quartz, chert, different clays and, in some cases, dolomite are generally present. Some secondary phosphate minerals can also be present, such as crandallite (Ca Al$_3$ (PO$_4$)$_2$ (OH)$_5$.H$_2$O), vivianite (Fe$_3$ (PO$_4$)$_2$.8H$_2$O) and brushite (Ca H PO$_4$.2H$_2$O).

A review of the spatial and temporal controls on the formation of sedimentary marine phosphate deposits was published recently by Cook (1984). An interesting account for the origin of marine phosphorites is given by Blatt and co-workers (1972).

Guano phosphates, once very important, account for less than 2 - 3% of today's world phosphate rock. They are formed directly or indirectly by the accumulation of bird droppings. Insular guano phosphate deposits are found in several islands in the different oceans. The largest known deposits are situated in Makatea (French Polynesia), Curacao (Dutch Antilles), Christmas Island, Nauru and Ocean Island (completely worked out). P$_2$O$_5$ grades can be as high as 42%.
4.1.5 - Infrared Spectroscopy and the Structure of Apatites

a) - Theoretical Considerations (Estep-Barnes, 1977):

The infrared absorption spectrum of a mineral is a plot of the amount of absorbed (or transmitted) radiation by the sample versus the wavelength (or frequency or "wavenumber") of the radiation employed. Absorption bands (peaks and shoulders) are produced in an infrared spectrum from the interactions of the radiation with the vibrations of the atoms or rotations of the molecular system (the latter is not possible in minerals). There are infrared active and inactive (or forbidden) vibrations. The active ones (which produce bands in the spectrum) occur when a dipole moment change happens during the vibration.

The specific band positions, intensities and shapes of absorption bands in the infrared spectrum of a mineral are determined by the relative masses, radii and co-ordination numbers of its constituent atoms, and by the distances, angles and bond forces between them. Thus, there are no two minerals that give exactly the same spectrum. The infrared spectrum of a mineral yields information regarding the crystal structure and bonding. It is sometimes as unique as an X-ray diffraction pattern.
The most predominant absorption bands in the infrared spectrum of a mineral are generally produced by the fundamental internal vibrations of isolated molecular groups or complex anions. For example, $\text{CO}_3^{2-}$, $\text{PO}_4^{3-}$ and $\text{SO}_4^{2-}$ give strong fundamental infrared bands at wavenumbers of approximately $1400-1599 \text{ cm}^{-1}$, $1000-1100 \text{ cm}^{-1}$, and $1100-1200 \text{ cm}^{-1}$, respectively. Weaker bands are due to combinations and overtones of the fundamentals, and to lattice (external) vibrations. It is possible to derive group frequency correlations which allow the immediate assignment of a mineral to a specific structural class, similar to the spectral-structural correlations extensively developed for functional groups in organic compounds.

The application of group-theoretical methods makes possible the assignment of absorption bands in the spectrum of a mineral to specific modes of vibration of its constituent atoms. The discussion of these and other methods is outside the scope of this work. They are discussed by Cotton, 1963 and Ferraro and Ziomek, 1969. The site-group analysis (Halford, 1946) which considers only molecular symmetry and disregards intermolecular interactions, can also be applied to molecular crystals such as carbonates, sulphates and phosphates.

The number of fundamental vibrations expected for a given molecular configuration of atoms is given by the formula $3N - 6$ where $N$ is the number of atoms in the configuration ($3N - 5$ for a linear group). For example,
for a phosphate group, which contains 5 atoms, the number of fundamental vibrations should be 9. Vibrations of atoms in various atomic configurations can be either stretching motions along or bending motions between bond axes. Stretching vibrations usually occur at much higher wavenumber than bending vibrations. It is common to use a $\nu_n$ symbolism to label the different vibrations. By convention the symmetric vibrations (stretching or bending) are labelled first in order of decreasing frequencies (wavenumbers). After assigning all symmetric vibrations, the asymmetric vibrations are labelled again also in order of decreasing frequencies. Generally, asymmetric stretching vibrations occur at higher frequencies than symmetric stretching vibrations. Further details can be found in Farmer (1974).

b) - Structure of Apatites (Montel et al., 1977; Young, 1980):

As previously seen (section 4.1.4), apatites possess an "open lattice". This type of lattice is responsible for the large number of substituents (impurities) found in most natural apatites.

The three most common Ca-apatites, viz. fluorapatite, hydroxyapatite and chlorapatite, crystallize in the hexagonal system. Apatites have a complex structure. They belong to
the dipyramidal hexagonal class, having a symmetry represented by the space group P 6/m (international symbolism). P refers to the primitive cell. 6/m means one hexad rotation symmetry axis and one reflection symmetry plane.

The unit cell contains 10 cations, 6 anions XO₄ and 2 anions Y. Figure 4.1a and b shows the position of these ions in the unit cell. In figure 4.1a (considering fluorapatite as an example), in the tetrahedral PO₄³⁻ ions, two of the oxygen atoms are in a horizontal plane, and the other two lie in the same vertical, thus superimposed in figure 4.1a. These ions are divided into two "groups", where they constitute hexagonal arrangements situated in terms of height at 1/4 and 3/4 of the unit cell.

Considering the structure parallel to the "c" axis (vertical), figure 4.1b shows the PO₄³⁻ ions in the form of "colonies", linked to each other in such a way that each phosphorus is bound to three oxygens in one "colony" and to one oxygen in a neighbor "colony".

In this structure one can find two types of "tunnels". One type of tunnel has a mean diameter of 2.5 Å. It is occupied in the case of Ca-apatites, by Ca²⁺ ions, called Ca(l), approximately at levels of 0 and 1/2 of the unit cell (these ions are not shown in figure 4.1b). The second type of tunnel is wider, with a mean diameter between 3 and 3.5 Å. Its centre is located at the hexad symmetry axis. It is very important in terms of physico-chemical
Figure 4.1 - Structure of Apatite (Young, 1980 and Montel et al., 1977)
(a) - Atomic arrangement in fluorapatite as seen in projection along "c";
(b) - Schematic representation of a tunnel of second type.
behaviour of apatites. It is surrounded by Ca$^{2+}$ ions, called Ca(2), arranged as equilateral triangles, situated at levels of 1/4 and 3/4 of the unit cell. This second type of tunnel is also surrounded by 4 other triangles formed by oxygens from neighbour $\text{PO}_4^{3-}$ ions. The Y ions (Cl$^-$, F$^-$, OH$^-$) are situated inside the tunnels of the second type. Their positions are indicated in figures 4.1b. F$^-$ lies at the centre of a triangle of Ca(2) ions, Cl$^-$ nearly at the centre of the triangle of oxygen ions, the oxygen O(H) of the hydroxyl ion lies about 0.4Å out of the plane of the Ca(2) triangle and the hydrogen lies 1Å further away, nearly in the plane of the nearest oxygen triangle.

In terms of the different substituents found in natural apatites, including deficient structures with holes, they are generally located in the tunnels. Cationic substituents are present in the smaller tunnels, in place of Ca(1) ions. The anionic substituents however, can be found inside the tunnels of the second type. Deficient apatites can also present holes (lack of stoichiometry), and these entities can also occur preferentially in tunnels of the second type. Other anionic substituents, especially those of the XO$_4$ type can replace the PO$_4$ groups. Nevertheless, CO$_3^{2-}$ can also replace the phosphate anion. Carbonate-apatites are classified as type A or B depending upon the position of the carbonate ion, whether inside the tunnel of the second type or replacing the phosphate group, respectively.
The peculiarities of the structure of apatites can promote significant changes in the physico-chemical behaviour of these minerals. The structure related effects in apatites have received considerable research effort in geological and biological sciences. The same cannot be said in the case of mineral processing. Further development in the area of flotation and other physico-chemical methods of mineral processing can probably be achieved if these structural effects are taken into consideration.

4.2 - Mining of Phosphate Ores (Notholt, 1973; McLellan, 1983; and Notholt and Hartley, 1983).

Both open pit and underground methods are used to mine phosphate ores. Most of the world's production comes from the open pit mining of sedimentary deposits. These deposits have varying thicknesses that may be less than 1m. In open pits a characteristic feature is the use of large, capital-intensive mining equipment such as electric walking draglines (25 - 30 m³ buckets) and bucket-wheel excavators. The use of this type of equipment enables low-grade phosphate beds to be worked economically. Conventional stripping, drilling, blasting, and extraction by bucket excavators and shovels is used in the majority of igneous deposits. Another characteristic feature of open pit operations is their large capacities, of the order of 2 to 3 million tonnes per year or more. Stripping of the overburden is done either by the
draglines themselves (e.g. Florida) or power shovels (e.g. Kola Peninsula, U.S.S.R.). A combined dredge/dragline operation is encountered in one case in North Carolina. Borehole mining has been tested in Northeastern Florida where the phosphate "matrix" is more than 76 m below the surface in waterbearing strata. More conventional open pit mines are found in Brazil, in the case of the carbonatitic ores.

Higher grade deposits in Morocco, U.S.S.R., Western U.S.A., Jordan and Tunisia are mined by different underground methods such as block caving (U.S.S.R.), continuous retreat room-and-pillar (Morocco), and sublevel stoping (U.S.A.).

4.3 - Flotation Beneficiation of Phosphate Ores

Flotation of phosphate minerals is affected by surface properties of these minerals, including surface electrical properties. The interaction between apatite and flotation reagents is dependent on the knowledge of the reactions taking place at the mineral/water interface.

4.3.1 - Apatite/Water Interface

Apatites can be considered as weak acid salts and have a very complex mechanism of charge generation (Parks, 1975). Lattice ions, e.g. Ca(II), $\text{PO}_4^{3-}$, $\text{F}^-$, and $\text{CO}_3^{2-}$, undergo hydrolysis controlled by pH. In a sense,
H$^+$ and OH$^-$, although not present in the lattice of these minerals (except OH$^-$ in the case of hydroxyapatite), can be considered together with the lattice ions as potential determining ions (pdi) (Smani et al., 1975) or at least as pdi of second order under Parks' (1975) concepts.

Somasundaran (1968) and Somasundaran and Agar (1972) showed that all lattice ions of fluorapatite greatly affect the zeta potential of this mineral. Somasundaran (1968) obtained an isoelectric point (iep) at pH 6 for a Canadian fluorapatite sample; this value was achieved only after weeks of equilibration. The method used was streaming potential. Non-equilibrium iep values were found to vary from pH 4 to the "equilibrium" iep (pH) of 6. The lattice ions added externally modified the zeta potential curves at pH values above and below the iep.

Saleeb and De Bruyn (1972) performed an exhaustive experimental programme involving the investigation of the effects of the different pdi for many synthetic apatite samples. They were the first to recognize explicitly the existence of a line of zero potential (or charge) in the solubility surfaces of these minerals (see discussion below). They also concluded that fluoride ions play a special role in controlling the electrophoretic behaviour of apatites, even though it is not a lattice ion (e.g., fluoride for hydroxyapatite). To account for this effect they proposed that ion exchange reactions take place, involving at least a monolayer of the solid surface.
Smani et al. (1975) measured iep (pH) for different natural apatite samples (sedimentary and igneous) and found that the values varied from 3.8 to 4.9, depending on the sample. They also showed that $H^+$, $OH^-$, Ca (II) and $-HPO_4^{2-}$ ions are pdi for this system. The surface charge generation mechanism was considered to be related to the hydrolysis of some lattice species and the adsorption of Ca(II) and $HPO_4^{2-}$ ions.

In recent investigations by Chander and Fuerstenau (1979 and 1984), equilibrium diagrams for the hydroxyapatite -water system were calculated. In these diagrams, they were able to define the theoretical line of zero charge (lzc). This line is plotted in the diagram shown in figure 4.2, which involves the concentration of all pdi as coordinates (actually the diagram is a bidimensional representation of a tridimensional construction). This mathematical treatment introduces the important fact that for minerals with such a complex structure as apatite ("tri-ionic"), the determination of iep and pzc values must always be accompanied by the proper experimental conditions of the tests. Also shown in this diagram are some of the published experimental iep and pzc values for hydroxyapatite, which are in fair agreement with the theoretical line of zero charge.
Figure 4.2 - The Position of the Calculated Line of Zero Charge (lzc) Shown by the Heavy Dashed Line. Also Shown Are Some Experimental pzc Values on the Solubility Surface of Hydroxyapatite (for details see original work by Chander and Fuerstenau, 1979).
Table 4.V shows a collection of the published values of iep (pH) and pzc (pH) for different types of apatites. The results obtained in the present investigation are included in the table for completeness but they will be discussed later. One important trend can be found in this table: all iep (pH) values are lower than the pzc (pH) values for the same type of apatite. In the case of hydroxyapatite, the average pzc (pH) is 8.3 and the average iep (pH) is 6.9. For fluorapaptite the situation is similar. The average pzc (pH) is 6.8 and the average iep (pH) is 5.0. These discrepancies can not be attributed only to experimental errors, different procedures and different samples (e.g. impurities and pre-treatment schemes). The theory is clear in stating (for example see Parks, 1975 and the IUPAC definitions given by Everett, 1972) that the pzc is defined as the negative logarithm of the pdi activity corresponding to zero true surface charge, $\sigma_0 = 0$. It is best determined by direct measurement of the adsorption densities of pdi (via a potentiometric titration technique, for example). Electrokinetic methods yield only the net charge, $\sigma_Z$, or the Zeta potential, $\zeta$, effective at the slipping or shear plane of the electrical double layer, and not the true surface charge of the potential. If $\sigma_0$ is zero but a specifically adsorbed ion is present, $\zeta$ will not be zero. Even in the absence of specifically adsorbed ionic species there may be source of potential, such as ion exclusion or oriented water molecules between the surface and the shear
## TABLE 4.V - Experimentally Determined iep(pH) and pzc(pH) for Apatites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>Molar Ca/P</th>
<th>Method</th>
<th>Electrolyte</th>
<th>iep or pzc</th>
<th>Equil. time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CaHA synthetic</td>
<td>1.59</td>
<td>m.e.</td>
<td>KNO₃</td>
<td>iep 7.4</td>
<td>30 minutes</td>
</tr>
<tr>
<td>2</td>
<td>CaHA</td>
<td>n.a.</td>
<td>m.e.</td>
<td>KNO₃</td>
<td>iep 7.0</td>
<td>24 hours</td>
</tr>
<tr>
<td>3</td>
<td>CaHA</td>
<td>1.636</td>
<td>m.e.</td>
<td>KCl</td>
<td>iep 6.8</td>
<td>24 hours</td>
</tr>
<tr>
<td>4</td>
<td>CaHA</td>
<td>1.636</td>
<td>m.e.</td>
<td>NaF</td>
<td>iep 6.8</td>
<td>24 hours</td>
</tr>
<tr>
<td>5</td>
<td>CaHA</td>
<td>1.67</td>
<td>m.e.</td>
<td>KNO₃</td>
<td>iep 7.0</td>
<td>overnight</td>
</tr>
<tr>
<td>6</td>
<td>CaHA</td>
<td>1.61</td>
<td>m.e.</td>
<td>NaNO₃</td>
<td>iep 6.5</td>
<td>n.a.</td>
</tr>
<tr>
<td>7</td>
<td>CaHA</td>
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<td>m.e.</td>
<td>-</td>
<td>iep 7.0</td>
<td>30 minutes</td>
</tr>
<tr>
<td>8</td>
<td>CaHA</td>
<td>1.66</td>
<td>p.t.</td>
<td>NaCl</td>
<td>pzc 7.6</td>
<td>n.a.</td>
</tr>
<tr>
<td>9</td>
<td>CaHA</td>
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<td>p.t.</td>
<td>KNO₃</td>
<td>pzc 8.5</td>
<td>16 hours</td>
</tr>
<tr>
<td>10</td>
<td>CaHA</td>
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<td>p.t.</td>
<td>KClO₄</td>
<td>pzc 8.5</td>
<td>16 hours</td>
</tr>
<tr>
<td>11</td>
<td>CaHA</td>
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<td>p.t.</td>
<td>NaCl</td>
<td>pzc 7.6</td>
<td>16 hours</td>
</tr>
<tr>
<td>12</td>
<td>CaHA</td>
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<td>p.t.</td>
<td>KCl</td>
<td>pzc 8.6</td>
<td>16 hours</td>
</tr>
<tr>
<td>13</td>
<td>CaHA</td>
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<td>p.t.</td>
<td>KCl</td>
<td>pzc 8.6</td>
<td>144 hours</td>
</tr>
<tr>
<td>14</td>
<td>CaHA</td>
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<td>p.t.</td>
<td>KCl</td>
<td>pzc 8.5</td>
<td>504 hours</td>
</tr>
<tr>
<td>15</td>
<td>CaHA</td>
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<td>KCl</td>
<td>pzc 8.3</td>
<td>16 hours</td>
</tr>
<tr>
<td>16</td>
<td>CaFA synthetic</td>
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<td>m.e.</td>
<td>KNO₃</td>
<td>iep 6.5</td>
<td>24 hours</td>
</tr>
<tr>
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<td>KCl</td>
<td>pzc 6.7</td>
<td>16 hours</td>
</tr>
<tr>
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<td>CaFA</td>
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<td>p.t.</td>
<td>KClO₄</td>
<td>pzc 6.8</td>
<td>16 hours</td>
</tr>
<tr>
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<td>CaFA</td>
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<td>p.t.</td>
<td>KCl</td>
<td>pzc 6.9</td>
<td>504 hours</td>
</tr>
<tr>
<td>20</td>
<td>CaFa nat. Canada</td>
<td>n.a.</td>
<td>s.p.</td>
<td>KNO₃</td>
<td>iep 4.0</td>
<td>hours</td>
</tr>
<tr>
<td>21</td>
<td>CaFA</td>
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<td>s.p.</td>
<td>KNO₃</td>
<td>iep 6.0</td>
<td>weeks</td>
</tr>
<tr>
<td>Sample No.</td>
<td>Description</td>
<td>Ca/P Method</td>
<td>Electrolyte</td>
<td>pH Method</td>
<td>iep or pzc</td>
<td>Equil. time</td>
</tr>
<tr>
<td>------------</td>
<td>-------------</td>
<td>-------------</td>
<td>-------------</td>
<td>-----------</td>
<td>------------</td>
<td>-------------</td>
</tr>
<tr>
<td>22</td>
<td>CaFA nat. Canada</td>
<td>n.a.</td>
<td>s.p.</td>
<td>KNO₃</td>
<td>iep 5.6</td>
<td>hours</td>
</tr>
<tr>
<td>23</td>
<td>CaFA ...</td>
<td>n.a.</td>
<td>pH ch.</td>
<td>KNO₃</td>
<td>pzc 7.0</td>
<td>up to 600 hr.</td>
</tr>
<tr>
<td>24</td>
<td>CaFA nat. Mexico</td>
<td>n.a.</td>
<td>m.e.</td>
<td>-</td>
<td>iep 6.4</td>
<td>n.a.</td>
</tr>
<tr>
<td>25</td>
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<td>n.a.</td>
<td>m.e.</td>
<td>NaClO₄</td>
<td>iep 5.6</td>
<td>n.a.</td>
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<tr>
<td>26</td>
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<td>m.e.</td>
<td>KCl</td>
<td>iep 4.0</td>
<td>n.a.</td>
</tr>
<tr>
<td>27</td>
<td>CaFA ...</td>
<td>1.688</td>
<td>pH ch.</td>
<td>KNO₃</td>
<td>pzc 6.0</td>
<td>n.a.</td>
</tr>
<tr>
<td>28</td>
<td>CaFA nat. Brazil</td>
<td>1.688</td>
<td>m.e.</td>
<td>-</td>
<td>iep 4.0</td>
<td>n.a.</td>
</tr>
<tr>
<td>29</td>
<td>CaFA nat. Sweden</td>
<td>1.68</td>
<td>m.e.</td>
<td>-</td>
<td>iep 3.0</td>
<td>15 minutes</td>
</tr>
<tr>
<td>30</td>
<td>CaFA nat. Brazil</td>
<td>1.688</td>
<td>m.e.</td>
<td>KCl</td>
<td>iep 4.1</td>
<td>30 minutes</td>
</tr>
<tr>
<td>31</td>
<td>CaFA ...</td>
<td>1.688</td>
<td>M&amp;R</td>
<td>KCl</td>
<td>pzc 7.0</td>
<td>30 minutes</td>
</tr>
<tr>
<td>32</td>
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<td>1.688</td>
<td>M&amp;R</td>
<td>KNO₃</td>
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<td>30 minutes</td>
</tr>
<tr>
<td>33</td>
<td>CaFA ...</td>
<td>1.688</td>
<td>pH ch.</td>
<td>KNO₃</td>
<td>pzc 7.0</td>
<td>up to 72 hr.</td>
</tr>
<tr>
<td>34</td>
<td>CaClA nat. Madag. 1.661</td>
<td>s.p.</td>
<td>KCl</td>
<td>iep 4.1</td>
<td>2 hours</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>CaClA nat. Aust.</td>
<td>n.a.</td>
<td>m.e.</td>
<td>NaClO₄</td>
<td>iep 6.7</td>
<td>30 minutes</td>
</tr>
</tbody>
</table>

---

36 **CO₃**-apatite  
   nat. Morocc | n.a. | s.p. | KCl | iep 4.7 | 2 hours  

37 **CO₃**-apatite  
   nat. Tunisia | n.a. | s.p. | KCl | iep 4.9 | 2 hours  

38 **CO₃**-apatite  
   nat. Algeria | n.a. | s.p. | KCl | iep 3.9 | 2 hours
### TABLE 4.V - Continued

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Description</th>
<th>Ca/P Method</th>
<th>Electrolyte</th>
<th>pH Value</th>
<th>Equil. Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>39</td>
<td>CO$_3$-apatite</td>
<td>n.a. m.e.</td>
<td>NaClO$_4$</td>
<td>iep 3.5</td>
<td>30 minutes</td>
</tr>
<tr>
<td></td>
<td>nat. Christmas</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Island</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>SrHA synthetic</td>
<td>m.e.</td>
<td>KNO$_3$</td>
<td>iep 9.8</td>
<td>24 hours</td>
</tr>
<tr>
<td>41</td>
<td>BaA synthetic</td>
<td>m.e.</td>
<td>KNO$_3$</td>
<td>iep 11.9</td>
<td>24 hours</td>
</tr>
</tbody>
</table>

**Notes:**
- CaHA - Calcium hydroxyapatite
- CaClA - Calcium chloroapatite
- BaA - Barium apatite
- m.e. - microelectrophoresis
- p.t. - potentiometric titration
- M&R - Mular and Roberts method

- CaFA - Calcium fluorapatite
- SrHA - Strontium hydroapatite
- CO$_3$-apatite - Carbonate-apatite
- s.P. - streaming potential
- pH ch. - pH change versus time
- n.a. - not available

**References - Sample No.:**
- Amankonah and Somasundaran, 1985 - 1
- Saleeb and De Bruyn, 1972 - 2, 3, 4, 16
- Chander and Fuerstenau, 1982 - 5
- Mishra et al., 1980 - 6
- Present work - 7, 30-33
- Bell et al., 1972 and 1973 - 8-15, 17, 18, 19
- Somasundaran, 1968 - 20, 21
- Somasundaran and Agar, 1972 - 22, 23
- Fuerstenau, M.C. et al., 1968 - 24
- Mishra, 1978 - 25, 35, 39
- Schulz and Dobias - 26, 27
- Coelho, 1984 - 28
- Pugh and Stenius, 1985 - 29
- Smani et al., 1975 - 34, 36-38
- Saleeb and De Bruyn, 1978 - 40, 41
plane. Therefore there is no guarantee that the true surface charge will be zero when electrokinetic potential is zero. Values of iep should be defined as the negative logarithm of pdi activity corresponding to zero electrokinetic potential.

To explain the difference observed between iep and pzc values presented in table 4. V, at pH values where the electrokinetic potential is zero, i.e. at the iep (pH), the surface should still carry a positive charge. This indicates that negative pdi can be specifically adsorbed inside the shear plane in such a way that the surface charge and the charge inside the shear plane compensate each other. Another aspect that should be considered is the kinetics of the apatite/water equilibrium. The increase in iep (pH) reported by Somasundaran (1968) as the equilibration time was increased, may be explained by the change of the concentration of pdi with time (analogous to a movement along the lzc line).

The effect of ionic species other than pdi on apatites is discussed later (see section 4.3.2.2).

4.3.2 - Interaction between Apatite and Flotation Reagents

Flotation plays a major role in the beneficiation of phosphate ores. This method is applied both to sedimentary ores (with siliceous gangue) and igneous ores (Hucut, 1982; Lawson et al., 1978).
4.3.2.1 - Apatite/Collectors

a) Anionic Collectors

Fatty acids are the most commonly used collectors in the beneficiation of phosphate ores. Because of their low cost and ready availability, they have been extensively used since the first plant operations in phosphate ore flotation. They confer, however, relatively low selectivity and require modifiers to be used in addition.

Sun et al. (1957) showed that the collecting power of fatty acids (in relation to phosphate minerals) increases as the degree of unsaturated bonds in the hydrocarbon chain increases up to a point. The collector order found was linoleic>oleic>linolenic>stearic. Tall oil, which is one of the most common industrially used collectors, is a mixture of linoleic, oleic and linolenic acids, having as impurity rosin acids. It is used in the form of emulsions (water and oil), saponified (NaOH) or neat.

Smani et al. (1975) studied the floatability of different apatites with sodium oleate. They observed that most apatites when floated with this collector showed two pH ranges of maximum floatability. The first, above pH 6, was associated with the chemisorption of oleate, resulting in the formation of Ca oleate on the surface. The second floatability maximum occurred close to the iep of the samples,
and physical adsorption of neutral oleate molecules was proposed. Mishra (1982), also studying the floatability with Na oleate of other different apatite samples, found only one pH range for maximum floatability. He proposed that the adsorption was due to a combination of chemical and hydrophobic bonds (formation of hemi-micelles). Figure 4.3 compares published microflotation results obtained in the flotation of different apatites with Na oleate at the 5 x 10^{-5} mol/litre concentration level as a function of pH (for references see figure caption). The analysis of this figure shows two important factors:

(i) - regardless of the mineral sample, high degrees of floatability are obtained in the medium alkaline pH range (approx. from pH 8 to pH 11);

(ii) - despite this general trend, the curves also show the importance of the source of the mineral.

Concerning the actual mechanisms involved in the interaction between Na oleate and the apatite surfaces, the following points deserve to be highlighted:
Figure 4.3 - Hallimond Tube Microflotation Results of Apatites in the Presence of \(5 \times 10^{-5}\) mol/litre Na Oleate as a Function of pH (1 - Silva et al., 1985; 2 - Smani et al., 1975).
(i) - there seems to be considerable evidence in favour of the formation of Ca oleate upon adsorption of oleate species (ions and molecules) as shown by Johnston (1969) and Johnston and Leja (1978);

(ii) - the importance of electrostatic forces in adsorption is probably minimal, although Hanna and Somasundaran (1976) claim that oleate adsorbs on apatite below the iep (pH) electrostatically, which does not imply in this author's opinion that the major adsorption driving force is electrostatic;

(iii) - Somasundaran and Ananthapadmanabhan (1986) claim that the interfacial activity of oleate dimeric species is five orders of magnitude greater than the monomeric oleate species in the pH range for maximum flotation of apatite. This pH range (approx. 8-9) coincides with the surface tension minimum of oleate aqueous solutions. Similar conclusions were reached by Pugh and
in a recent work, Moudgil et al. (1986) proposed that surface precipitation of Ca oleate is the predominant mechanism for the observed hydrophobicity of apatite particles. Simultaneous molecular adsorption (independent of the solid/solution ratio) and surface precipitation occurred in a region of the adsorption isotherm corresponding to solute concentrations below bulk precipitation conditions at pH 10. The readers are referred to the original work for details;

the second flotability peak observed by Smani et al. (1975) was interpreted as physical adsorption of neutral oleic acid molecules by the authors. However, it has not been observed in any other instance and may be related to the impurities (calcite ?) in the samples used by these workers.
case. Other anionic surfactants such as Na dodecyl sulphate, phosphonic acid, sulphonates and sulphonates have been studied as alternative collections for apatite, especially for difficult to treat calcite/dolomite bearing phosphate ores (Hanna and Somasundaran, 1976, Collins et al., 1984 and Neves, private communication, 1986). In these cases the work performed so far is not sufficient to draw any conclusions regarding the mechanisms involved in the adsorption of these collectors on apatite surfaces.

b) Cationic Collectors

The problem of beneficiating carbonate sedimentary phosphate has been the subject of a considerable amount of study without much success (Soto and Iwasaki, 1984 and 1986). One of the promising methods proposed for this type of ore involves the use of aliphatic primary amines in a mildly acidic pulp, as an apatite collector (Snow, 1979 cited in Soto and Iwasaki, 1986). The method also uses a non-polar hydrocarbon (ancillary collector) and has been successfully piloted (Lawver et al., 1978).

Industrially, cationic collectors are used in the beneficiation of phosphate ores in reverse circuit to float off residual siliceous gangue, entrained and/or entrapped during the anionic apatite flotation step. This technique has been in use for more than 40 years in Florida, U.S.A. ("double flotation").
Mishra (1979) investigated the effects of
dodecylamine hydrochloride in both the electrokinetic and
floatibility behaviour of apatite. His results could be
fitted by the electrostatic/hemi-micelle model of Gaudin and
Fuerstenau (1955). Hanna and Somasundaran (1976) also give
support to this mechanism. However, more recent
investigations of Soto and Iwasaki (1984 and 1986) presented
experimental evidence in favour of a chemical model of
adsorption in which amine ions react with surface phosphate
ionic sites on apatite, due to the chemical affinity between
this pair of ions. In other words, the chemical interaction
appears to have an overriding influence on the collector
action, although the electrostatic interaction (and the
formation of hemi-micelles) may play a role in the total free
energy of adsorption. Thermochemical adsorption measurements
associated with studies on the solubilities of
phosphate/amine salts(*) support the chemical model.

A closer look at the results of Smani et al. (1975)
for a cationic collection would also indicate that the
electrostatic model could not explain their data completely.
The microflotation curves presented show a considerable
decrease in floatability of apatite at pH values where the
net surface charge is negative and increasing in absolute

(*) One simple way to appreciate the low solubility of this
type of compound is to introduce a small amount of an alkyl
amine solution to a phosphate based pH buffer. The
precipitate forms rather quickly and is quite visible.
value.

Taggart and Arbiter (1944) had proposed an ion exchange mechanism (involving the formation of an insoluble salt between amine and phosphate) for the interaction between amines and apatites. The available evidence now seems to favour this formerly discredited mechanism.

c) Amphoteric Collectors

Amphoteric collectors possess simultaneously cationic and anionic functions, according to the working pH. This type of collector is used industrially in Finland to float an igneous phosphate ore (Kiukkola, 1980). In the Finnish application, the amphoteric collector is an N-sarcosin and only the anionic function of the surfactant is used in the direct flotation of apatite. Houot et al. (1985) used a series of amphoteric collectors (alkyl amino propionic acid, alkyl propylene diamino propionic acid, alkyl dipropylene triamino propionic acid and alkyl dipropylene triamino dipropionic acid) in their studies of the flotation of sedimentary phosphate ores (dolomitic and argillaceous gangue). In their testwork, the amphoteric collectors successfully played the roles of cationic and anionic collectors in circuits resembling the conventional "double flotation" circuits already mentioned. The major advantage of the amphoteric collectors in this case is the elimination of the wash/scrubbing step, necessary to remove fatty acid
coating on apatite.

4.3.2.2 - Apatite/Modifiers

A large variety of modifiers, both organic and inorganic are used in the flotation of phosphate ores. They can act as pH modifiers, activators, depressants, froth controllers, complexants, etc. but their roles and mechanisms of interaction are not clearly established in most cases. The need for such reagents is very significant, and without them, selective separation would not be possible.

The effects of pdi species have been already discussed (section 4.3.1). The effect of different inorganic modifiers such as Na silicates and Na-tripolyphosphate was investigated in more detail in a few papers. Mishra (1978) using Na metasilicate with SiO$_2$/Na$_2$O ratio 1 : 1, showed that the zeta potential of a Christmas Island apatite increased from about -30mV to about -40mV at pH 11 in the presence of 1.2g/l of the reagent. Parsonage et al. (1984) used a different Na silicate with a 1.35 : 1 SiO$_2$/Na$_2$O ratio, but also reported a change in the zeta potential of the fluorapatite at pH 9.5 from -18mV to -45mV in the presence of .5g/l of the reagent. They concluded that Na silicate dispersed fluorapatite by forming a protective layer of hydrophilic silicate. The mechanisms of adsorption are not well explained yet. According to Marinakis and Shergold (1985) Na silicate monomeric species are chemisorbed on
calcite. The ionic monomers would interact with Ca sites at the surface and a similar mechanism could be expected for apatites. Mishra (1978) studying the system apatite/calcite/oleate/metasilicate concluded that there was preferential adsorption of silicate on calcite at pH 10. However, Parsonage et. al (1984) showed that if apatite is conditioned with silicate in the presence of calcite, flotation of both minerals with oleate is depressed by the silicate species. Mishra (1978) also proposed that hydrogen bonding between surface atoms and OH groups of silicate aqueous species would play an important role in the overall adsorption driving force.

Parsonage et al. (1984) also obtained a large increase in the negative value of the zeta potential of apatite on the presence of Na tripolyphosphate (-80mV at pH 9.5 in the presence of 1g/l of the reagent). Rao et al. (1985) observed selective depression of apatite by potassium orthophosphate in a carbonated ore at acidic conditions. The adsorption of orthophosphate would take place via reaction between Ca sites and phosphate ions, CaHPO$_4$. Johnston and Leja (1978) suggested that the selective depression of apatite by orthophosphate/water occurs by hydrogen bonding on apatite surfaces. At the same pH, dolomite and calcite surfaces would generate CO$_2$ via dissolution, disturbing the formation of the layer, thus permitting the adsorption of oleate species.
Aquino et al. (1987) obtained improved selectivity in the separation of apatite/carbonate using phosphoric acid at pH 5.5 as compared to sulphuric acid at the same pH, in the reverse carbonate flotation with oleic acid.

The depressant effect of cations (other than pdi) is also of interest. Coelho (1984) reported that Al aqueous species depressed the Na oleate floatability of both calcite and apatite. The same effect is reported in the literature for other cations (Hanna and Somasundaran, 1976). The cause for the depressant action is normally related to the formation of complexes between cation and collector species. However, their actual mechanisms still need to be described.

The most accepted model for the interaction between metallic ionic species and mineral surfaces is that of James and Healy (1972). This model predicts that upon reacting these metallic species with minerals, charge reversals will take place. The first charge reversal (CR1) is the mineral iep (pH). The second charge reversal (CR2) is related to the adsorption of the metallic ionic species, more specifically its first hydroxo-complex. Charge reversal 3 (CR3) is associated with the return to negative surface charge at pH values where the metallic ionic species are anionic in character (hydrolyzed). Details of this model are also given by Senior (1987).
The combined effect of sodium silicate/cations is even less well understood. Klassen and Mokrousov (1963) presented experimental results of the combined effect of cation/sodium silicate on the recovery of Ca-minerals (fluorite, calcite, scheelite and apatite) with oleic acid at pH 9.1 - 9.5. In the absence of cations but in the presence of 1.5 kg/t Na-silicate, all minerals displayed recoveries above 95%. In the presence of 300 g/t Al(SO$_4$)$_3$ scheelite and apatite were preferentially depressed, while in the presence of MgSO$_4$ scheelite and calcite were the two minerals most affected (apatite recovery remained unchanged in this case).

In the case of cationic flotation, anions such as phosphate and sulphate are found to produce activation effects. Cations promote depression in most cases. Again the mechanisms are not well understood in these cases. Apparently phosphate and sulphate increase the adsorption of cationic collectors (Hanna and Somasundaran, 1976).

The adsorption of polymers and similar compounds on apatites (except starches that will be dealt with later, see section 4.5.4) was studied in a few cases. Pradip and co-workers (1980) investigated the adsorption of polyacrylamides on fluorapatite and hydroxyapatite. For a slightly anionic polyacrylamide (SEPARAN NF 10) adsorption appears to result mainly from hydrogen bonding between -OH groups on the apatite surface and -CONH$_2$ groups of the polyacrylamide macromolecules. Electrostatic forces are
also involved, since adsorption decreased as the pH increased (thus the negative value of the zeta potential).

Belton and Stupp (1983) investigated the adsorption of ionized poly (acrylic acid) on tribasic Ca phosphate surfaces. They concluded that the adsorption behaviour was affected significantly by the substrate's electrostatic potential as well as the polymer conformation and intermolecular association in solution.

4.4. - Starches

4.4.1. - Composition and Structure

Starch is a very important polysaccharide. It is a natural polymer formed by the condensation of α-D(+) GLUCOSE molecules (see figure 4.4a). The starch macromolecule consists of α-D(+) glucose monomers, polymerized chiefly by 1 → 4-α and 1 → 6-α linkages. It occurs as granules whose shape and size are characteristic of the plant from which the starch is derived. The chain length and molecular weight of the starch also depend upon its source. Several books and articles are available and cover the subject in great depth (e.g. Whistler and Smart, 1953; Radley, 1953; Whistler and Paschal, eds., 1965; Whistler, ed., 1964; Greenwood, 1970; Danishefsky et al., 1970; Be Miller, 1973; Powell, 1973; Satterthwaite and Iwinski, 1973; Kennedy and White, 1979; Whistler, 1980;
and Whistler et al., eds., 1984).

A review on the relevant aspects of starches and derivatives is presented in the next sections. Generalities included in this review were obtained mainly from the references listed above.

Starch Fractions

In general, starches contain about 20% of a linear fraction called AMYLOSE and 80% of a branched fraction termed AMYLOPECTIN. A strong evidence of the branched nature of starch comes from the fact that end group analysis suggests an average chain-length of 24 to 30 glucose units for a starch molecule (Hough and Jones, 1954). An unbranched molecule with 24-30 glucose units would present a maximum molecular weight (see next section) of 4860, while starches have much larger molecular weights.

The two starch fractions, viz. amylose and amylopectin, are both made up of α-D(+) glucose but differ in molecular shape, size and extent of contaminants. Amylose is the macromolecule resulting chiefly from 1 → 4-α linkages (Figure 4.4b). On the other hand, amylopectin is a larger, macromolecule resulting from branching, through 1 → 6α linkages (Figure 4.4c) of 1 → 4-α linear chains. Its structure is tree-like, with many of the branches themselves having sub-branches. The amylose content of various starches
Figure 4.4 - Schematic View of (a) Glucose (monomer), (b) Amylose and (c) Amylopectin (polymers) (Leja, 1982).
Amylose and amylopectin have substantially different properties. Many of these differences are derived from differences in molecular weight and molecular shape (structure of the macromolecule). Amylose, usually characterized by its straight chain nature gives a deep blue color when its solutions are reacted with iodine. Hanes (1937) and Freudenberg et al. (1939) were the first to propose a helical structure for amylose in aqueous solutions. The deep blue coloration with iodine is a result of the complexation of iodine inside the helical structure of amylose. Iodine is occluded within the helix, to form clathrate structures. Amylopectin also reacts with iodine, but the intensity and wavelength of the color developed by this reaction are different (much lower intensity at a lower wavelength).

In their native state, starch granules are crystalline and exist in three polymorphic forms, namely A-starch of cereals and grains, B-starch of tubers and roots, and C-starch of various beans, smoothed pea and banana. These polymorphic forms have been identified by X-ray diffraction. Sarko and Wu (1978) claim that the crystalline structures of starches are largely due to the linear amylose fraction. From their studies they found that both A- and B- amylose have virtually identical conformation: both are right-handed, parallel-stranded helices, differing in the crystalline packing of the helices and the water
TABLE 4.VI - Amylose Content of Various Starches
(approximate values)(*)

<table>
<thead>
<tr>
<th>Starch</th>
<th>Amylose Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alderman pea</td>
<td>65</td>
</tr>
<tr>
<td>Amylomaize</td>
<td>52</td>
</tr>
<tr>
<td>Apple</td>
<td>19</td>
</tr>
<tr>
<td>Arrowroot</td>
<td>21</td>
</tr>
<tr>
<td>Babacu nut</td>
<td>22</td>
</tr>
<tr>
<td>Banana</td>
<td>16-17</td>
</tr>
<tr>
<td>Barley</td>
<td>22</td>
</tr>
<tr>
<td>Buckwheat</td>
<td>28</td>
</tr>
<tr>
<td>Cashew nut</td>
<td>24</td>
</tr>
<tr>
<td>Canna</td>
<td>26</td>
</tr>
<tr>
<td>Chick pea</td>
<td>33</td>
</tr>
<tr>
<td>Corn (commercial)</td>
<td>26</td>
</tr>
<tr>
<td>Easter lily</td>
<td>31</td>
</tr>
<tr>
<td>Horse chestnut</td>
<td>26</td>
</tr>
<tr>
<td>Iris tuber</td>
<td>27</td>
</tr>
<tr>
<td>Mango kernel</td>
<td>24</td>
</tr>
<tr>
<td>Oat</td>
<td>27</td>
</tr>
<tr>
<td>Parsnip</td>
<td>11</td>
</tr>
<tr>
<td>Pea (smooth-seeded)</td>
<td>35</td>
</tr>
<tr>
<td>Sago</td>
<td>26</td>
</tr>
<tr>
<td>Sorghum</td>
<td>27</td>
</tr>
<tr>
<td>Steadfast pea</td>
<td>67</td>
</tr>
<tr>
<td>Sugary mutant corn</td>
<td>70</td>
</tr>
<tr>
<td>Sweet potato</td>
<td>20</td>
</tr>
<tr>
<td>Tapioca</td>
<td>18(17)</td>
</tr>
<tr>
<td>Tulip</td>
<td>26</td>
</tr>
<tr>
<td>Waxy corn</td>
<td>0-6</td>
</tr>
<tr>
<td>Waxy barley</td>
<td>3</td>
</tr>
<tr>
<td>Waxy sorghum</td>
<td>0</td>
</tr>
<tr>
<td>Wheat</td>
<td>25</td>
</tr>
<tr>
<td>White potato</td>
<td>23(20)</td>
</tr>
</tbody>
</table>

(*) Two important factors control the apparent amylose content in any starch: primarily genetic factors (e.g. waxy starches which consist almost exclusively of amylopectin); second, maturity of the plant at the time of starch isolation (amylose content increases with increased maturity) (Greenwood, 1970).
content. The A-amylose crystallizes in an orthogonal unit cell with 8 water molecules per unit cell. On the other hand, B-amylose crystallizes in a hexagonal unit with 36 water molecules per unit cell. The C-structure is a mixture of A- and B- unit cells, being intermediate between the A- and B- forms in packing. Starch precipitated from solution, or complexed with various organic molecules, adopts the so-called V-structure ("Verkleisterung"). Theoretical calculations have shown that V-amylose is more stable as a left-handed helix than as a right-handed one (Rao et al., 1967 and Whistler and Daniel, 1984). The relevance of the structural aspects of starch will become clear in the results and discussion chapter.

4.4.2 - Molecular Weight

Difficulties in molecular weight determinations of polysaccharides are increased in the case of starches not only because starches are usually two component mixtures, but also because of the marked tendency of the molecules to associate or retrograde.

The majority of molecular weight measurements were made on separated amylose and amylopectin fractions. Table 4.VII shows a compilation for some of the available data, indicating the technique used for the determination. As seen in this table, the ranges of molecular weight for both amylose and amylopectin are very wide.
TABLE 4.VII - Molecular Weight of Starch Fractions (after Young, 1984)

<table>
<thead>
<tr>
<th>Parent Starch</th>
<th>Method(*)</th>
<th>M.W. range ((1 \times 10^{-6}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A) AMYLOSE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potato</td>
<td>O.P.</td>
<td>0.082-0.113</td>
<td>Whistler and Smart(1953)</td>
</tr>
<tr>
<td>Potato</td>
<td>L.S.</td>
<td>0.49</td>
<td>Young(1984)</td>
</tr>
<tr>
<td>Wheat</td>
<td>O.P.</td>
<td>0.09-0.16</td>
<td>Whistler and Smart(1953)</td>
</tr>
<tr>
<td>Wheat</td>
<td>L.S.</td>
<td>0.34</td>
<td>Young(1984)</td>
</tr>
<tr>
<td>Corn</td>
<td>U.C.</td>
<td>0.017-0.25</td>
<td>Whistler and Smart(1953)</td>
</tr>
<tr>
<td>Corn</td>
<td>O.P.</td>
<td>0.08-0.3</td>
<td>Whistler and Smart(1953)</td>
</tr>
<tr>
<td>Tapioca</td>
<td>O.P.</td>
<td>0.3</td>
<td>Whistler and Smart(1953)</td>
</tr>
<tr>
<td>Barley</td>
<td>V.M.</td>
<td>0.30</td>
<td>Young(1984)</td>
</tr>
<tr>
<td>Potato(***))</td>
<td>L.S.</td>
<td>0.146-2.25</td>
<td>Everret and Foster(1959)</td>
</tr>
<tr>
<td>Potato(***))</td>
<td>L.S.</td>
<td>0.16-2.29</td>
<td>Banks and Greenwood(1963)</td>
</tr>
<tr>
<td>B) AMYLOPECTIN</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potato</td>
<td>O.P.</td>
<td>0.36</td>
<td>Whistler and Smart(1953)</td>
</tr>
<tr>
<td>Potato I(***))</td>
<td>L.S.</td>
<td>440.00</td>
<td>Young(1984)</td>
</tr>
<tr>
<td>Potato II(***))</td>
<td>L.S.</td>
<td>6.50</td>
<td>Young(1984)</td>
</tr>
<tr>
<td>Tapioca</td>
<td>L.S.</td>
<td>450.00</td>
<td>Young(1984)</td>
</tr>
<tr>
<td>Waxy Corn</td>
<td>L.S.</td>
<td>400.00</td>
<td>Young(1984)</td>
</tr>
<tr>
<td>Waxy Corn Sheared</td>
<td>L.S.</td>
<td>10.00</td>
<td>Young(1984)</td>
</tr>
<tr>
<td>Wheat</td>
<td>L.S.</td>
<td>400.00</td>
<td>Young(1984)</td>
</tr>
<tr>
<td>Corn</td>
<td>O.P.</td>
<td>0.3</td>
<td>Whistler and Smart(1953)</td>
</tr>
</tbody>
</table>

Notes: (*) O.P. = osmotic pressure; L.S. = light scattering; V.M. = viscosity; U.C. = ultracentrifugation
(**) Fractioned amylose samples
(***) Two different cultivars of the same plant
Regardless of the technique and the great variability of the molecular weight results shown in table 4.VII, the molecular weight of amylose is an order of magnitude smaller than that of amylopectin. The linear configuration of amylose as compared to the branched amylopectin molecule is one of the reasons for its lower molecular weight.

Light scattering derived molecular weights are probably closer to the real values as indicated by some of the more recent determinations (Young, 1984). One example of the discrepancies among the methods is given in table 4.VII. The osmotic pressure molecular weight measurement quoted by Whistler and Smart (1953) for potato amylopectin is 360,000 daltons as compared to the 65 and 440 million daltons given by Young (1984), determined by light scattering. Potato amylopectin is one of the largest natural polymers known.

Another aspect is that osmotic pressure and chemical end-group analysis yield number-average molecular weights (Mn). Light scattering methods yield weight-average molecular weights (Mw). The number-average molecular weight loses significance for broad molecular weight distributions (as in the case of starch fractions), since it is not sensitive to large molecules. In turn, light scattering methods are not sensitive to small molecules. The ratio Mw/Mn gives an indication of the extent of the molecular weight distribution (Young, 1984). Viscosity related methods are not absolute and are dependent on calibration from
osmometry or light scattering (to obtain the constants $K$ and $\alpha$ of the Mark-Howink equation - see section 5.3.5).

A curious and important result also presented in table 4.VII deals with the effect of shearing on molecular weights of starches. Non-sheared waxy corn amylopectin gave a molecular weight (Mw) of 400 million daltons whereas the same sample subjected to shearing (not described in the original reference) gave a molecular weight 40 times smaller. Shearing of polymer solutions is known to effect their flocculation power (Halverson and Panzer, 1978).

4.4.3 - Minor Constituents

Starch is composed of carbon, hydrogen, and oxygen on the ratio of 6 : 10 : 5 (empirical formula $(C_6H_{10}O_5)_x$). When starch is subjected to hydrolysis by acids and/or certain enzymes, it yields glucose. It is, therefore, consider a condensation polymer of glucose. The theoretical values for carbon, hydrogen and oxygen in % by weight are the following: 44.4% C, 6.2% H and 49.4% O.

In addition to carbohydrate, starch grains contain minor consituents which can influence their properties. The most important are lipids (fatty acids such as stearic, palmitic, oleic and linoleic acids and lysophospholipids), phosphorus (bound-esterified or in the form of adsorbed phosphatides) and nitrogen (generally in the form of proteins). Starches also contain small amounts of inorganic
contaminants (less than 0.5% by wt.). Davies et al. (1980) presents an extensive list of starches and corresponding contaminant levels. Proteins are generally associated with the amylose fraction whereas phosphorus is more related to amylopectin. Potato starches have the highest phosphorus content among common starches (0.071% P) and tapioca starches the lowest (0.003% P).

4.4.4 - Solution Preparation and Retrogradation

As already mentioned different solvent systems have been used to prepare aqueous dispersions (solutions) of starches. Two methods of gelatinization\(^1\) are commonly used for the preparation of starch - thermal and chemical gelatinization. Gelatinization temperatures depend on the amylopectin content of the starch. High amylopectin content is associated with low gelatinization temperatures, for example 55 - 66°C for potato, 62 -72°C for corn and 67.5 -74°C for waxy sorghum. Chemical (or cold) gelatinization can be used. Strong alkalis are the most common reagents used. Sodium hydroxide has the lowest critical gelatinization level (lowest consumption). The combination of thermal and chemical gelatinization can also be used.

\(^{(1)}\) Gelatinization is the process by which the strong intermicellar network of starch granules is weakened by disrupting hydrogen bonds. The resultant paste is water soluble.
Retrogradation is a spontaneous phenomenon that occurs in aqueous solutions of starches. When they are allowed to stand (under aseptic conditions), they become opalescent, increasingly cloudy and lower in viscosity. Finally, they undergo precipitation. Amylose retrogrades faster than amylopectin. Therefore starches with higher amylopectin content form more stable solutions (e.g. waxy corn starch, constituted of almost 100% amylopectin retrogrades less than 10% in 100 days whereas corn starch retrogrades approximately 60% in 30 days). Amylose retrogradation takes only a few hours. Retrogradation rate is increased by lowering the temperature (Whistler and Smart, 1983).

4.5 - Selective Flocculation and the Use of Starches in Mineral Processing

The treatment of fine mineral particles has received special attention in the last 10 to 15 years (see for example the special volumes edited by Somasundaran and Arbiter, 1979; and Somasundaran, 1980). The reasons for such interest are related to two basic facts:

(i) - Fine particles cannot be efficiently separated by any of the conventional beneficiation processes.
(ii) - exploitation of lower grade ores with fine liberation sizes generates large tonnage of difficult to concentrate fine particles.

Selective aggregation\(^1\) of valuable fines is desirable because larger units are more easily concentrated (Fuerstenau et al., 1979). Another advantage is that a finer impoverished stream, containing mainly the waste particles, is produced.

Selective flocculation by polymers has been a widely studied technique to achieve selective aggregation. Haseman patented a selective flocculation process for phosphate fines in 1953. His findings are discussed elsewhere in this thesis (see the section dedicated to the selective flocculation of phosphates). Selective flocculation is based upon the creation of a set of physico-chemical conditions (Yarar and Kitchener, 1970; and Friend and Kitchener, 1973):

(i) - to increase the degree of dispersion of waste minerals\(^2\).
(ii) - to destroy the dispersion stability of

\(^1\) Aggregation is used here as a general term. An aggregate of loose structure, formed (generally) by the addition of organic polymers should be referred to as a "floc". An aggregate formed by compression of electrical double layers (generally more compact than a floc) should be called a "coagulum".

\(^2\) Reverse selective flocculation is also possible, for example waste clays in a sylvinite ore are selectively flocculated and floated (Banks, 1979).
valuable minerals through selective adsorption of a selective flocculant.

(iii) - promote the growth of flocs mainly constituted of valuable minerals.

4.5.1 - Basic Principles

In principle the method is very simple. Figure 4.5 schematically shows the essential steps involved in selective flocculation of a hypothetical two phase ore (Read and Hollick, 1976). Firstly inorganic dispersants (or less frequently low molecular weight organic polymers) are added to the ore pulp to ensure that no heterocoagulation will take place. In the real case dispersants would be added, most probably, to the grinding mill where fresh surfaces are created and cross-contamination of mineral particles can occur. Secondly, a high molecular weight organic polymer is added which is selectively adsorbed on one of the minerals. Thirdly collision processes result in floc formation. Finally the flocs settle while the particles of the dispersed mineral remain in suspension. Flocculated and dispersed phases can then be separated by different means.
Figure 4.5 - Fundamental Stages in the Selective Flocculation of a Two-Phase Ore (Read and Hollick, 1976).
Selective adsorption of polymers (followed by selective flocculation) is only achieved if the different mineral particles in an ore pulp are properly dispersed. Dispersion is the first pre-requisite for selective flocculation.

The stability of colloidal dispersions is of special interest in many fields. Colloid chemists have been studying the phenomena related to this stability for over a century.

In an aqueous dispersion of particles, attractive interactions arise from London dispersion forces. These long-range forces are one of the types of the so called van der Waals attractive forces. The other two types, Keesom and Debye interactions, do not contribute to the long-range attraction between colloidal particles (Napper, 1983). Hamaker (1937) extended the classical London's treatment of the dispersion forces between atoms to calculate those between colloidal particles. The potential energy ($V_A$) of interaction between two spherical particles of the same material is then given by:

$$V_A = -A \frac{a_1 a_2}{6(a_1 + a_2)} H_0$$  \hspace{1cm} (EQ. 4.5.1)

where

- $A = \text{Hamaker constant}$
- $a_1, a_2 = \text{radii of the respective particles}$
- $H_0 = \text{shortest distance between the surfaces}$
of the two particles.

The Hamaker constant depends on the polarizing properties of the molecules comprising various components of the system. For example for the quartz/water/quartz system, \( A = 1 \times 10^{-13} \) erg (Healy, 1979).

Naked and uncharged colloidal particles undergo very rapid coagulation effected by long-range attractive forces. To stabilize a colloidal dispersion it is necessary to provide long-range counteracting repulsion forces between the particles. At the present time (Napper, 1983) there are two ways to impart stability to colloidal dispersion: electrostatic stabilization and polymeric stabilization.

The first type is dealt with by the Derjaguin-Landau-Verwey-Overbeek (D.L.V.O.) theory. The interaction of two disimilar electrical double layers (*) gives rise to an expression for the repulsive energy of interaction \( V_R \) as follows (Hogg et al., 1966):

\[
V_R = \frac{\varepsilon a_1 a_2 (\psi_{01}^2 + \psi_{02}^2)}{4(a_1 + a_2)} \left\{ \frac{2\psi_{01} \psi_{02}}{\psi_{01}^2 + \psi_{02}^2} \ln \left[ \frac{1 + \exp(-kH_0)}{1 - \exp(-kH_0)} \right] + 1 \ln(1 - \exp(-2kH_0)) \right\}
\]

(EQ 4.5.2)

(*) For reviews of double layer theories and applications see for example Parks (1976), Hiemenz (1977), Leja (1982), Lyklema (1982), Usui (1984).
where $\varepsilon =$ dielectric constant of the suspending medium
$a_{1,2} =$ radii of the respective particles (assumed spherical)
$H_0 =$ shortest separation distance
$\psi_{01,02} =$ Stern potential of the respective double layer
(generally assumed to be equal to the zeta potential)
$k =$ Debye-Huckel reciprocal length parameter, given by
$k^2 = 8 \frac{cez^2}{eKt}$, where:
$c =$ concentration (ions/cm$^3$)
e = electronic charge
$K =$ Boltzmann's constant
$T =$ absolute temperature
$z =$ ionic charge

The above relationship for $V_R$ is general. However, it holds only for magnitudes of $\psi_{01}$ and/or $\psi_{02}$ of less than 25mV and for solution conditions such that the double layer "thickness" is small compared to the particle size. Hogg and co-workers (1966) point out that the given relationship is a good approximation for $\psi_{01}$ and $\psi_{02}$ less than 50 - 60 mV.

The total energy of interaction can then be expressed in a very simplified way as follows:

$$V_T = V_A + V_R \quad \text{(EQ. 4.5.3)}$$
Using a sign convention such that negative $V_T$ leads to coagulation, in the case of two identical particles, stabilization will occur when $V_R > V_A$, since $V_A$ is always negative (attractive). Homocoagulation occurs when the identical particles are uncharged ($V_R = 0$). In a system consisting of particles of species A and B, the phenomenon of heterocoagulation can take place when the particles of species A are negatively charged and particles of species B are positively charged or uncharged (and vice-versa).

The above discussion demonstrates the importance of surface charge on the stability of colloidal dispersions. The same phenomena occur in suspensions of fine mineral particles. In ore pulps, where many mineral species are present, the validity of treatments such as the D.L.V.O. theory is limited. The real systems are complicated by a number of factors, for example the variety of the size and shape of particles and the presence of many ionic species introduced by the partial dissolution of some minerals during milling operations. The basic principles, however, apply. Heterocoagulation must be avoided by adequate addition of dispersants. Selective coagulation is possible under very controlled conditions (see for example a review paper by Laskowski, 1982). Parsonage et al., 1982, applied the D.L.V.O. theory to their studies of slime coating with considerable success.
Colloidal dispersions can also be stabilized by polymeric compounds. Steric stabilization (Napper, 1983) is imparted by the macromolecules that are attached to the surfaces of the particles. This type of phenomenon is also known as the "protective colloid" stabilization. A combination of electrostatic and steric stabilization (electrosteric stabilization) can occur. For details on polymeric stabilization see Napper (1983). Examples of the use of acrylate polymers for the stabilization (dispersion) of dolomite fines are given by Van Lierde (1974).

4.5.3 - Dispersants

The simplest and most widely used dispersants are pH modifiers - most minerals being strongly negatively charged in an alkaline media. By pH regulation, the $V_R$ term in the energy equation is increased because the zeta potential on the particles is increased. A very simple rule-of-thumb (Zeta-Meter manual, 1975) is that excellent dispersion is achieved when all particles in an aqueous environment have zeta potentials greater than 60mV (calculated by the Helmholtz-Smoluchowski equation).

The presence of different ionic species in ore pulps is one of the possible reasons that pH control alone is sometimes not sufficient to impart a high degree of dispersion. Additional dispersing reagents (inorganic compounds and less frequently organic) have to be used.
Sodium silicates with different SiO₂ : Na₂O ratios are frequently used (Rabone, 1936; Gaudin, 1957; Sollenberg and Geenwalt, 1958; Hines and Vincent, 1962; Smith and Songstad, 1962; Klassen and Mokrousov, 1963; Fuerstenau et al., 1968; Falcone Jr., 1982; Leja, 1982; Krishanan and Iwasaki, 1982, to cite a few). Most uses of sodium silicates are in flotation systems, as depressants for oxide and salt-type minerals. Although these reagents are widely used, little is known about the mechanisms of their action.

Commercial sodium silicates can be described by a general formula: NaₘH₄ₘSiO₄, where m denotes the average number of OH⁻ bound per Si atom and varies from 0.5 to 1.6. In aqueous solutions, sodium silicate can exist as a variety of species:

Si(OH)₄ (uncharged), SiO(OH)₃⁻, SiO₂(OH)₄⁴⁻, Si₂O₄(OH)₄²⁻ and Si₄O₈(OH)₄⁴⁻.

The first 3 species are monomeric, the fourth is dimeric and the last tetrameric. Polymeric species are also known to form (Leja, 1982 and Falcone, 1982).

Some important characteristics of the action of sodium silicates are:

(i) - they impart highly negative surface charges on different minerals.
(ii) they can reverse zeta potential of minerals which have been in contact with ions such as Ca\(^{2+}\), Mg\(^{2+}\) and Fe\(^{3+}\).

(iii) they can form insoluble surface precipitates with the ions mentioned above (Krishnan and Iwasaki, 1982).

Given these characteristics one can speculate upon the possible mechanisms involved in the dispersion (and depression) promoted by sodium silicates. One of the possibilities is a mechanism similar to the electrostatic stabilization described by Napper (1983). The polymerized sodium silicate species would adsorb on the mineral surface through hydrogen bonding or depending on the mineral, through covalent bonding with cations on the surface (forming compounds such as Ca-silicates). In fact, Krishnan and Iwasaki (1982) have used a scanning transmission electron microscope to show the formation of Ca-silicate on the surface of quartz, previously treated with Ca ions.

Sodium polyphosphates are also common dispersants (Conley, 1974 and Leja, 1982). Sodium pyrophosphate, containing the multivalent P\(_2\)O\(_7\) anion is an example of a linear-chain polyphosphate which can be represented by a general formula \((P_nO_3n+1)^{(n+2)^{-}}\). Pyrophosphate is present in solution as dimeric species. Sodium hexametaphosphate is a cyclic polyphosphate, containing the multivalent P\(_6\)O\(_{18}\) anion. Calgon (trade name), one of
most common commercial dispersants, is a mixture of hexametaphosphate and pyrophosphate (Leja, 1982).

Polyphosphates are capable of precipitating $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ as insoluble phosphates. Their dispersing action may be partially related to this phenomenon. However they also react with the mineral surfaces imparting high negative charge to them. In this way they act as electrostatic stabilizers. Competition with collector species such as sulphonate and fatty acids, is one of the suggested roles of polyphosphate as depressants for dolomite and calcite (Hanna and Somasundaran, 1976). More recently, Yongxin and Changgen (1983) and Changgen and Yongxin (1983), investigated the effect of various polyphosphates on the flotation of scheelite, calcite, fluorite, garnet and quartz with sodium oleate. They found that pyrophosphate and hexametaphosphate were effective depressants for calcite and fluorite, and depressed scheelite only weakly. Furthermore they concluded that the selective dissolution of calcite and fluorite was related to the selective depression of Ca ions caused by the polyphosphates. This dissolution would reduce the availability of adsorption sites for the collector (sodium oleate) on these minerals. The reason for the selective action was considered to be related primarily to the crystal structure of the mineral. No detectable adsorption of polyphosphate species on the minerals studied was observed.
4.5.4 - (Selective) Destabilization of Mineral Suspensions

When polymers are added to an aqueous suspension of particles, an extra term in the total energy of interaction equation is introduced:

\[ V_T = V_A + V_R + V_B \]  \hspace{1cm} (EQ. 4.5.4)

Where \( V_B \) is the interaction energy caused by "bridging". For most purposes \( V_B \) can be considered a component of \( V_A \). The bridging mechanism is shown in Figure 4.6 for the cases of partial and complete coverage. It was first proposed by Ruehrvein and Ward (1952) and Michaels and Morelos (1955). Medium to high molecular weight polymeric adsorbates with several active sites on them can induce aggregation by attaching themselves to two or more particles. Such bridging between particles will particularly occur under conditions where the particles are not completely coated by the polymeric species (see Figure 4.6b). According to Healy and La Mer (1964), maximum flocculation and filtration rates occur when the fraction of particle surface covered by polymer molecules is close to 0.5. Somasundaran (1980) points out that complete coverage (Figure 4.6a) can also induce flocculation. Excess coverage can lead to steric stabilization.
(a) COMPLETE COVERAGE,

\[ \Delta G_I = \Delta H_I - T \Delta S_I \]

increase from released solvent molecules;
decrease from interpenetrating polymers

Flocculation under complete coverage is possible only if the free energy of interpenetration of adsorbed layers, \( \Delta G_I \), is negative.

(b) PARTIAL COVERAGE

Figure 4.6 - Flocculation by Polymers under Complete and Partial Coverage Conditions (Somasundaran, 1980).
The second pre-requisite for selective flocculation is the selective adsorption of polymer molecules on the valuable minerals\(^{1}\). Very high molecular weight polymeric flocculants, frequently used for clarification of process water, are usually nonselective (Laskowski, 1982).

The mechanisms of adsorption of flocculants have been described in the literature (see for example Yarar and Kitchener, 1978; and Somasundaran, 1980). In summary, the forces involved in the adsorption of polymers are:

(i) - electrostatic bonding
(ii) - hydrogen bonding
(iii) - covalent bonding

Electrostatic forces are predominant in the adsorption of polymers with a large number of charged units. Both anionic and cationic polymers are commonly used in mineral processing. Hydrogen bonding is probably present in almost every case of polymer adsorption on oxygen bearing minerals. This can be the predominant mechanism for the adsorption of non-ionic (or slightly anionic) polymers. Covalent bonding occurs when active groups of the polymer interact with cations of the mineral surface. Michaels and Morelos (1955) proposed that the adsorption of polyacryla-

(1) As already mentioned, "reverse" selective flocculation can also be used (see also Cormode, 1985).
mides on kaolin was due to the formation of salt-type compounds by reaction between the polymer anionic groups and the $\text{Ca}^{2+}$ ions present on kaolin surface. Another example of covalent bonding is the adsorption of cellulose xanthate polymers on minerals such as chalcopyrite (Attia and Kitchener, 1975; Sresty, Raja and Somasundaran, 1978).

Of special interest to this study is the adsorption of starches and derivatives. Iwasaki and co-workers (see for example Iwasaki and Lai, 1965; Balajee and Iwasaki, 1969; Iwasaki and Lipp, 1971) extensively investigated the adsorption (and flocculation) of modified and non-modified starches on quartz, goethite and hematite. Figure 4.7 shows two typical adsorption isotherms for corn starch and cationic starch on both quartz and hematite. The figure also shows the pH dependence of adsorption. Assuming that both mineral surfaces are capable of hydrogen bonding with all types of starches (non-ionic, anionic, and cationic), and the molecular weight of all starches is equivalent, the contribution of hydrogen bonding for their adsorption on the mineral should also be equivalent. In Figure 4.7 it is readily apparent that corn starch is more strongly adsorbed on hematite than on quartz, but the adsorption density of the cationic starch is higher on quartz than on hematite. On closer examination of the individual isotherms, it will be noted that the adsorption of corn starch decreases with increasing pH, whereas that of cationic starch increases with increasing pH. Quartz is more electronegative than hematite.
Figure 4.7 - Adsorption of Corn Starch (a) and Cationic Starch (b) on Hematite (H) and Quartz (Q) (Balajee and Iwasaki, 1969).
in aqueous suspensions in the pH range 7 to 11. Corn starch is negatively charged in this range and the cationic starch is positively charged. The diametrically opposite adsorption behaviour of corn starch and cationic starch on these two oxide minerals can be understood if an electrostatic interaction exists between the starches and mineral surfaces.

Using the experimental facts discussed above, Figure 4.8 schematically shows a model for the mode of adsorption of various starches on oxide minerals, incorporating hydrogen bonding and electrostatic interaction (attraction or repulsion).

The isotherms shown in Figure 4.7 exhibit an extra characteristic, likely not determined by electrostatic interactions. The adsorption densities for both starches on hematite (corn and cationic) are much larger than the adsorption densities of corn starch on quartz. Although an electrostatic component is evident from the results shown, the starches clearly displayed a greater specificity for hematite, even when the surface of hematite was only slightly negative (the isotherm at pH 7 for cationic starch on hematite shows a saturation adsorption density of approx. 1 mg per m² compared to corn starch on quartz, which at the same pH, shows a maximum adsorption density of approx. 0.3 mg per m²). Another important difference is the shape of the isotherms for hematite. The curves are typical for cases where the polymer has a very high affinity for the surface, showing a steep rise in the adsorption density at
low concentration (Lipatov and Sergeeva, 1971). These isotherms also reach the saturation coverage at low concentrations. Similar adsorption isotherms of other polysaccharides on different minerals are reported in the literature. In most cases this high affinity type of isotherm was considered to be caused by some sort of covalent bonding occurring between ionic groups on the polymer and cations on the mineral surface. In recent research by Solari et al. (1985), the adsorption of carboxymethylcellulose (CMC) on untreated and acid-leached graphite samples was investigated. The untreated graphite presented adsorption isotherms of the high affinity type whereas for the acid-leached sample a low-affinity type was observed and much smaller densities were obtained. The strikingly different behaviour of the two graphite samples (regarding CMC adsorption) was considered to be related to cationic impurities (mainly Ca, Mg and Fe) on the surface of the untreated graphite. These impurities would be preferred adsorption sites for CMC molecules where strong covalent bonding could take place.

Somasundaran (1969) investigated the adsorption of corn starch (gelatinized with 0.5M NaOH) on calcite. The adsorption isotherms were of the high affinity type and the adsorption density decreased with the increase of pH (similar to the adsorption behaviour of corn starch on hematite). He also measured the total calcium concentration in calcite suspensions as a function of residual (equilibrium) starch
Figure 4.8 - A Model Showing Mode of Adsorption by Various Starches on Negatively Charged Oxide Mineral Surfaces (Balajee and Iwasaki, 1969)
concentration, and found that Ca solubility (at a fixed pH) increased as the starch concentration increased. Complex formation between starch and surface calcium species can therefore be considered as an adsorption mechanism for the calcite-starch system. Starch impurities, such as fatty acid and phosphate can be involved in the adsorption mechanism. Ionization of starch hydroxyls (pK 12) could also contribute to the complexation reactions involving Ca surface species.

Khosla et al. (1984) also concluded that the interaction between starch and calcite (as well as between starch and hematite) is of a chemical nature. Their thermochemical studies for starch/calcite and starch/hematite systems indicated that the adsorption of starch macromolecules on the surfaces of these minerals is an exothermic process. Desorption testwork also demonstrated the partial irreversability of adsorption, further indicating the high affinity of the polymers for the surfaces in question.

Steenberg and Harris (1984) also studied the adsorption of a modified potato starch (FLOCGEL 100) on various minerals, including apatite. The adsorption isotherm for apatite/FLOCGEL 100 at pH 7 showed a plateau region starting at approximately 12 mg/l. They concluded that hydrogen bonding was the main adsorption mechanism operating in this system, based only on the shape of the isotherm and on the similar behaviour displayed by different minerals regarding the adsorption of starch.
4.5.5 - Flocculant Applications

It is outside the scope of the present work to discuss flocculants other than polysaccharides, especially starches. An extensive review of flocculating agents was published by Halverson and Panzer (1978). Most polymers used as flocculants by the mineral industry today are synthetic. Polyacrylamides, polyamines and poly(ethylene oxides) are some typical examples. Rogers and Poling (1978) discussed the composition and performance of some commercial polyacrylamides.

Starches were the most commonly used flocculants by the mineral industry before the advent of synthetic polymers. Gardner et al. (1939) tested 25 different organic raw materials (most of them starches or containing starches) as flocculants for coal tailings. They noticed that, depending on the preparation of the flocculant solution, the starches tested were very effective. Potato starch, causticized with NaOH, gave the best results.

The interest in starches as flocculants and depressants grew considerably after the early studies of Gardner and co-workers (1939). Flotation of iron ores received most of the research on starches (Cooke et al., 1952; Chang et al., 1953; Chang, 1954; Iwasaki and Lai, 1965; Iwasaki, 1965; Colombo and Rule, 1967; Iwasaki et al., 1969; Balajee and Iwasaki, 1969; Iwasaki and Lipp, 1971; Colombo
and Frommer, 1976; and Jacobs and Colombo, 1981). In almost all of these studies starches (modified and non-modified) were found to act as (selective) depressants for hematite and other iron oxides during the reverse flotation of quartz and other silicates. The reverse flotation techniques used were either cationic (with amines) or anionic (Ca activation followed by carboxylate flotation).

Starches were also extensively used in studies of the selective flocculation of iron ores (Frommer, 1968; Balajee and Iwasaki, 1969; Iwasaki et al., 1969; Colombo and Frommer, 1976; Colombo, 1977; Colombo, 1979; Iwasaki, 1979; Chen and Leja, 1980; Colombo, 1980; Jacobs and Colombo, 1980; Paananen and Turcotte, 1980; Abu Rashid and Smith, 1982; Guraraj et al., 1983; Zuleta et al., 1984; Coelho, 1984; and Hunamantha Rao and Narasimhan, 1985). The most important industrial application of selective flocculation (as a selective desliming operation) is encountered in the beneficiation of iron ores (Tilden Mine, U.S.A). As in the case of depression, starches selectively adsorb and flocculate iron oxides. Solution preparation procedures were also found of critical importance.

Starches and derivatives were also used for the selective flocculation of coal fines (e.g. Zuleta et al., 1985), depression of coal (e.g. Im and Aplan, 1981; Miller et al., 1983), flocculation of phosphate slimes (La Mer and Smellie, 1956 a and b) and selective flocculation of
phosphate fines and ores (see separate section for discussion of this topic). The results of La Mer and Smellie (1956 a,b) are particularly interesting because of one of their conclusions. They tested different starches and found potato starch was the most effective. They concluded that the reason for the superior performance of potato starch was the presence of esterified phosphate groups in the flocculant (recall that Gardner et al. (1939) also found potato starch to be the most effective starch flocculant). Coelho (1985) also reported potato starch as being the most effective depressant for an apatitic iron ore.

4.5.6 - Effect of Dissolved Species on Adsorption and Flocculation

Adsorption (or "abstraction") of aqueous metallic species on minerals is known to cause major changes in their surface properties. In a classical work, James and Healy (1972) proposed a model for the adsorption of aqueous metallic species on mineral substrates. According to their model, hydrolysable metal ions (such as those derived from Al, Fe(III), Co(II), Ca(II) and Mg(II) salts) adsorb on a mineral surface independently of the surface charge, but adsorption is greatly influenced by pH, concentration of the
salt and, to a lesser extent, by the nature of the surface. In terms of zeta potentials, most mineral systems present at least two points of zero potential (the iep and a point of zeta reversal). For minerals with an iep in the acidic range of pH, two points of zeta reversal can be identified.

The interaction of starches and other flocculants with mineral surfaces is strongly affected by adsorption of hydrolysable metal ions. For example Iwasaki et al., 1980; and Heerema et al., 1983, investigated a system involving Ca and Mg ions, starch and quartz. They found that both ions increased the adsorption of starch on quartz (and consequently its flocculation). Increased flocculation of quartz by starch was maximal at pH values close to that required for precipitation of Ca and Mg hydroxides. Presence of such ions in hematite-quartz systems caused poor selectivity in both selective flocculation and flotation operations. Similar behaviour was found for the Al-starch-quartz-hematite system (de Araujo, 1982; de Araujo and Coelho, 1984). The presence of these ubiquitous ions in ore pulps can be related to poor selectivity obtained in some studies with real ores as compared to pure mineral systems.

4.5.7 -Selective Flocculation Of Phosphates

Table 4.VIII summarizes the reported attempts to flocculate selectively phosphate ores and fines. The following paragraphs will give a more detailed account of the
major findings in each case.

Haseman (1953) was the first to patent a process of selective flocculation for phosphate fines. In that early time he recognized the need for increasing the overall recovery of phosphate ores from Florida, being treated by the desliming-double flotation technique. Corn starch, solubilized by heating was used as (selective) flocculant for apatite. Adequate dispersion was achieved by controlling the pH with NaOH. The example given in this patent demonstrates that selective flocculation of fines was able to increase the overall P\textsubscript{2}O\textsubscript{5} recovery by at least 10%. Stated differently, the application of flocculation in this case was equivalent to recovering fines down to 1μm in size.

Later Davenport and co-workers (1969) also applied selective flocculation to phosphate fines. They used a non-specified starch to flocculate selectively a -53 μm phosphate slime, also from Florida. The +53 μm was floated conventionally. Although they were able to recover 75%P\textsubscript{2}O\textsubscript{5} from the slime, both enrichment ratio and selectivity were poor. They concluded that, because of economic considerations and high R\textsubscript{2}O\textsubscript{3} of their selective flocculation concentrate, the use of the technique for the sample tested was not a viable alternative to improve recovery.
TABLE 4.VIII - Selective Flocculation of Phosphate Ores and Minerals.

<table>
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<tr>
<th>ORE TYPE</th>
<th>FLOCCULANT(S)</th>
<th>DISPERGANT(S)</th>
<th>pH</th>
<th>F K K D</th>
<th>GRADE</th>
<th>CONCENTRATION</th>
<th>GRADE</th>
<th>X P O 4</th>
<th>GRADE</th>
<th>X P O 4</th>
<th>RECOVERY REFERENCES(S)</th>
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<tbody>
<tr>
<td>Unspecified (-10 um)</td>
<td>Corn Starch (heating &amp; agitation)</td>
<td>NaOH</td>
<td>19</td>
<td>9.4</td>
<td>0.94</td>
<td>32.33</td>
<td>8.84</td>
<td>50</td>
<td></td>
<td></td>
<td>Hassman, 1953</td>
</tr>
<tr>
<td>Hard rock phosphate slime, from Florida (-33 um)</td>
<td>Starch</td>
<td>NaOH</td>
<td>20</td>
<td>10.0</td>
<td>N.A.</td>
<td>15.0</td>
<td>N.A.</td>
<td>70</td>
<td></td>
<td></td>
<td>Davenport et al., 1969</td>
</tr>
<tr>
<td>Scrubbed matrix from Florida</td>
<td>Strongly Antidote Corn Starch</td>
<td>NaOH and Na₂SIO₃</td>
<td>9.4</td>
<td>10.0</td>
<td>N.A.</td>
<td>15.0</td>
<td>N.A.</td>
<td>70</td>
<td></td>
<td></td>
<td>Colombo, 1976</td>
</tr>
<tr>
<td>Unspecified phosphate fines (-45 um)</td>
<td>Carboxymethyl starch</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1) Degree of substitution (D.S.) of 0.06</td>
<td>NaOH and Na₂SIO₃ (SIO₃/Na₂O) = 3.5</td>
<td>9</td>
<td>23.6</td>
<td>9.94</td>
<td>32.33</td>
<td>8.84</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td>Beudet et al., 1960</td>
</tr>
<tr>
<td>2) D.S. of 0.06</td>
<td>do. [7.5 kg/t]</td>
<td>9</td>
<td>23.6</td>
<td>9.94</td>
<td>33.05</td>
<td>N.A.</td>
<td>46.8</td>
<td></td>
<td></td>
<td></td>
<td>Ibid.</td>
</tr>
<tr>
<td>3) D.S. of 0.40</td>
<td>do. [10 kg/t]</td>
<td>9</td>
<td>23.6</td>
<td>9.94</td>
<td>30.75</td>
<td>N.A.</td>
<td>70.0</td>
<td></td>
<td></td>
<td></td>
<td>Ibid.</td>
</tr>
<tr>
<td>4) D.S. of 0.40</td>
<td>do. [12.5 kg/t]</td>
<td>9</td>
<td>23.6</td>
<td>9.94</td>
<td>31.55</td>
<td>N.A.</td>
<td>54.8</td>
<td></td>
<td></td>
<td></td>
<td>Ibid.</td>
</tr>
<tr>
<td>5) D.S. of 0.06</td>
<td>NaOH and Na pyrophosphate [1 kg/t]</td>
<td>9</td>
<td>23.6</td>
<td>9.94</td>
<td>29.75</td>
<td>N.A.</td>
<td>51.96</td>
<td></td>
<td></td>
<td></td>
<td>Ibid.</td>
</tr>
<tr>
<td>6) D.S. of 0.06</td>
<td>NaOH and Na₂SIO₃ [15 kg/t]</td>
<td>9</td>
<td>26.10</td>
<td>8.53</td>
<td>31.60</td>
<td>5.02</td>
<td>39.83</td>
<td></td>
<td></td>
<td>Ibid.</td>
<td></td>
</tr>
<tr>
<td>7) D.S. of 0.40</td>
<td>do. [15 kg/t]</td>
<td>9</td>
<td>26.10</td>
<td>8.53</td>
<td>32.95</td>
<td>4.23</td>
<td>58.90</td>
<td></td>
<td></td>
<td>Ibid.</td>
<td></td>
</tr>
<tr>
<td>Carboxymethyl cellulose, D.S. of 0.7 [0.15 kg/t]</td>
<td>NaOH and Na₂SIO₃</td>
<td>N.A.</td>
<td>25.06</td>
<td>9.24</td>
<td>30.80</td>
<td>4.29</td>
<td>50.63</td>
<td></td>
<td></td>
<td>Ibid.</td>
<td></td>
</tr>
</tbody>
</table>
TABLE IV - VIII - Cont.

<table>
<thead>
<tr>
<th>ORE TYPE</th>
<th>FLOCCULANT(S)</th>
<th>DISPERGANT(S)</th>
<th>pH</th>
<th>FLOATED GRADE</th>
<th>CONCENTRATE GRADE</th>
<th>RECOVERY REFERENCES(S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sedimentary phosphate ore from Brasil†</td>
<td>Corn Starch (gelatinized with NaOH)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1) -12 μm</td>
<td>NaOH [1 kg/t]</td>
<td>9</td>
<td>4.3</td>
<td>N.A.</td>
<td>5.0</td>
<td>N.A.</td>
</tr>
<tr>
<td>2) -12 μm</td>
<td>NaOH [1 kg/t]</td>
<td>10</td>
<td>4.3</td>
<td>N.A.</td>
<td>7.0</td>
<td>N.A.</td>
</tr>
<tr>
<td>3) -45 μm</td>
<td>NaOH [1.5 kg/t]</td>
<td>10.5</td>
<td>6.3</td>
<td>N.A.</td>
<td>11.0</td>
<td>N.A.</td>
</tr>
<tr>
<td>4) -105 μm</td>
<td>NaOH [1.2 kg/t]</td>
<td>10.2</td>
<td>10.3</td>
<td>N.A.</td>
<td>11.5</td>
<td>N.A.</td>
</tr>
</tbody>
</table>

| Sedimentary phosphate ore from Brasil† | Corn Starch (gelatinized with NaOH) | | | | | |
| 1) -300 μm ground ores [1 kg/t] | NaOH and Na metasilicate [0.5 kg/t] | 10.5 | 26.2 | 12.7 | 11.2 | 29.6 | N.A. | 92.0 | Coelho, 1984 and de Araujo et al., 1986 |
| 2) -106 μm ground ores [1 kg/t] | do. | 10.5 | 26.2 | 12.7 | 11.2 | 29.6 | N.A. | 80.3 | Ibid. |
| 3) -45 μm ground ores [1 kg/t] | do. | 10.5 | 26.2 | 12.7 | 11.2 | 29.6 | N.A. | 82.0 | Ibid. |

| Pure minerals (hydroxypatite, calcite and quartzes) | Superfloc 16 or A-100 (polyacrylamide, H.M. = 4 x 10⁶) [16 g/t] hydroyxypatite and calcite only | | | | | |
| 1) Superfloc 16 or A-100 (polyacrylamide) [0.625 kg/t] and Na₂SiO₃ [1 kg/t] | Cyquest (Na polyacrylate) | 10.2 | 14.65 | - | 29.24 | - | 84.69 | Rubio and Harabini, 1985 |
| 2) do., hydroxyapatite/calcite/quartzes | do. | 10.2 | 12.3 | - | 25.5 | - | 88.4 | Ibid. |

NOTES:
1. $X_R\text{O}_3 = X \text{Fe}_2\text{O}_3 + 3X\text{Al}_2\text{O}_3$; maximum acceptable between 4 and 51.
2. Concentrate Grade refers to average grade or best grade obtained for the flocculated phase.
3. N.A. = Not Available.
4. Flotation was used to increase grade of flocculated phase.
5. These ores are from the same area as the ore studied by de Oliveira and Coas, 1982. Minerals present in these ores are francolite, quartz, kaolinite, micas, and iron hydroxides.
Colombo (1975) investigated the selective flocculation of a scrubbed low grade phosphate slime, again from Florida. A strongly anionic corn starch was used in conjunction with sodium silicate and NaOH (pH 9.4). Recovery was as high as 75%P$_2$O$_5$ but the concentrate assayed only 15%P$_2$O$_5$, from a feed grade of approximately 10%P$_2$O$_5$.

Baudet and co-workers patented in 1980 the use of carboxymethyl starch with different degrees of substitution (D.S.) as a selective flocculant for phosphate slimes (-45 μm). In their work, sodium silicate with a SiO$_2$/Na$_2$O ratio of 3.5:1 was used in combination with NaOH (pH 9) as dispersant. They were able to concentrate the slimes, which assayed 23.6 to 26.1%P$_2$O$_5$, to a grade generally higher than 30%P$_2$O$_5$. The %R$_2$O$_3$ reported in some tests were below 5%. Recoveries varied considerably, from 46.8 to 70%P$_2$O$_5$. The best results were achieved by using at least 10kg/t of Na$_2$SiO$_3$ and 4 - 5kg/t of modified starch with a D.S of 0.40.

Despite the fact that Haseman recognized the potential for selective flocculation being used as a selective desliming technique, only very recently has this idea been tested for phosphates. In 1974 the first industrial application of selective flocculation (as a desliming operation) went into production. Some pioneering work on phosphate ores from Brazil was performed by Coelho (1976 and 1979). In 1982, de Oliveira and Gomes utilized, with limited success, the combination of selective flocculation-flotation.
in their attempts to concentrate a low grade Brazilian phosphate ore (10%P₂O₅). After testing selective flocculation alone for different size fractions, they performed some preliminary anionic flotation tests on the selectively deslimed product (or "selective flocculation pre-concentrate"). Although they were able to increase considerably the grade of this product by flotation (up to 26.5%P₂O₅), flotation recoveries were poor (47 of 54%P₂O₅).

More recently, Coelho (1984) and de Araujo et al. (1986) reported the use of the selective flocculation-flotation technique in an attempt to concentrate three different sedimentary phosphate ores, also from Brazil. Table 4.IX summarizes their findings. Especially for the lower grade ores (12.4 and 17.6%P₂O₅), the use of this beneficiation scheme seemed very attractive. Overall recoveries were as high as 83.4%P₂O₅, after the rejection of 23 to 27% of the ore mass as slimes. These slimes for the two lower grade ores tested, assayed less than 4.5%P₂O₅ and represented a maximum loss of 8.3%P₂O₅. As pointed out in these works, no attempts to optimize flotation of the selectively deslimed product were made.

Another recent contribution in this field is the work of Rubio and Marabini (1985). They addressed a more complex subject, involving the selective flocculation of apatite from calcite. As previously mentioned, most of the future phosphate ores will have calcite (or another
carbonate) as a major gangue mineral. They were able to flocculate selectively hydroxyapatite from calcite using Na polyacrylate as a (selective) dispersant for calcite and a polyacrylamide (superfloc 16) as flocculant for apatite. When quartz was present, Na silicate in conjunction with Na acrylate were used as dispersants.

In conclusion, selective flocculation applied to phosphate ores and minerals has given relatively encouraging results, in small scale testing. Reasons for the apparent lack of interest by industry in attempting to apply the technique, are related to the low value of phosphate rock and to the existence of relatively large reserves of high grade phosphate ores with low mining and beneficiation costs. However, lower grade deposits will have to be utilized in the near future. Exploitation of lower grade ores is inherently associated with the need for highly efficient processing techniques. Besides that, as shown in a recent work by Scheiner and Smelley (1985) for the Florida phosphate industry, disposal regulations are becoming more severe every year. In Florida for example, new State regulations restrict the current method of disposal of slimes, which is impoundment behind earthen dams. If selective desliming is able to increase mass recovery for instance by 10%, the reduction in costs of disposal will probably make selective flocculation an economic alternative. The best utilization of known resources from non-renewable sources such as minerals should also be always considered.
<table>
<thead>
<tr>
<th>SAMPLE/ (Feed Grade)</th>
<th>SLIMES</th>
<th>FLOCCULATED PRODUCT*</th>
<th>FLOTATION CONCENTRATE†</th>
<th>FLOTATION TAILINGS</th>
</tr>
</thead>
<tbody>
<tr>
<td>HG/ (26.2% P₂O₅)</td>
<td>16.8</td>
<td>21.4</td>
<td>29.4</td>
<td>32.3</td>
</tr>
<tr>
<td></td>
<td>21.4</td>
<td>13.5</td>
<td>78.6</td>
<td>52.3</td>
</tr>
<tr>
<td></td>
<td>13.5</td>
<td>86.5</td>
<td>23.2</td>
<td>63.0</td>
</tr>
<tr>
<td></td>
<td>23.2</td>
<td>63.0</td>
<td>23.7</td>
<td>26.3</td>
</tr>
</tbody>
</table>

| MG/ (17.6% P₂O₅)    | 4.2    | 23.1                 | 21.2                   | 30.2              |
|                      | 23.1   | 5.6                  | 76.9                   | 47.7              |
|                      | 5.6    | 94.4                 | 83.4                   | 11.0              |

| LG/ (12.4% P₂O₅)    | 3.9    | 26.8                 | 15.8                   | 27.3              |
|                      | 26.8   | 8.3                  | 73.2                   | 35.9              |
|                      | 8.3    | 91.7                 | 79.1                   | 12.6              |

* calculated figures
† considering losses of the selective flocculation (recoveries considering flotation alone are: HG = 73.2, MG = 88.4 and LG = 86.3)

TABLE 4 IX - Selective Flocculation(Corn Starch,1 kg/t)/Flotation of Sedimentary Phosphate Ores(de Araujo et al.,1986).
5 - EXPERIMENTAL

5.1 - Preparation of Mineral Samples

Natural and synthetic mineral samples were used in the present work. Among the different apatite samples available, a fluorapatite from Monteiro, Brazil was chosen. It was available in enough quantity as hand picked crystals. The other available apatite samples included: fluorapatite from Durango, Mexico (green crystals), fluorapatite from Ontario, Canada (blue, massive), and carbonate-apatite containing iron, from Itataia, Brazil (brown powder, previously ground). Details on these samples are given in Appendix I, since they were not used extensively in the experimental work. Besides these natural apatites, a synthetic hydroxyapatite was also used in a few experiments. This sample is a tribasic calcium phosphate from Fisher Scientific (A.C.S. certified reagent).

The following non-apatitic samples were also utilized in the present work: quartz from Ottawa, Canada (supplied as crystals by the Mines Branch); Min-U-Sil-5, a 99.7% SiO₂ synthetic silica sample, non-porous; kaolinite, "air floated kaolin", from Georgia, USA. More details on these samples are also given in Appendix I. Among the non-apatitic samples, quartz was selected for the majority of the comparative tests.
Table 5.1 presents the results for the chemical analyses performed on the two natural mineral samples most frequently used. These results were obtained using different analytical techniques, listed in the same table. Both minerals have very high degrees of chemical purity. As expected, the fluorapatite sample has more contaminants than the quartz sample. As previously discussed in the review section (4.1.4), this is a consequence of the open lattice of the apatites. The relatively high grades for Th, La and U were also expected due to the local geology.

The two natural minerals (fluorapatite from Monteiro and quartz from Ottawa), were crushed in three stages using conventional laboratory crushers. After crushing to d50 of about 1 cm, the samples were subjected to a low intensity magnetic separation (with a hand magnet) to remove any wear debris from the crushing operations. After that they were subjected to wet grinding in a pebble filled ceramic mill, at 60% solids, obtained by the addition of distilled water (pH 5.5 - 5.8). The grinding operation was performed in stages of 30 minutes followed by wet screening on a 38 micron sieve. The oversize of the screen was added to a new batch of unground material and another 30 minute grinding stage was then initiated. After a number of stages, the grinding was stopped. The plus 38 micron material was dried and screened. The -212 + 150 micron size fraction was kept for the microflotation testwork. The -38 micron fraction, after a 12 hour settling period, was dried overnight at 80°C and kept
TABLE 5.1
CHEMICAL CHARACTERIZATION OF MINERAL SAMPLES

<table>
<thead>
<tr>
<th>CONSTITUENTS</th>
<th>UNITS</th>
<th>METHOD</th>
<th>FLUORAPATITE</th>
<th>QUARTZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>F$_2$O$_5$</td>
<td>%</td>
<td>wet assay</td>
<td>40.5</td>
<td>0.03</td>
</tr>
<tr>
<td>CaO</td>
<td>%</td>
<td>wet assay</td>
<td>54.01</td>
<td>0.04</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>%</td>
<td>wet assay</td>
<td>0.014</td>
<td>0.06</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>%</td>
<td>wet assay</td>
<td>0.057</td>
<td>0.07</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>%</td>
<td>wet assay</td>
<td>0.27</td>
<td>99.56</td>
</tr>
<tr>
<td>F</td>
<td>%</td>
<td>i.s.e. (*)</td>
<td>2.60</td>
<td>n.a.(**)</td>
</tr>
<tr>
<td>Cl</td>
<td>%</td>
<td>Xray flu.(***)</td>
<td>0.38</td>
<td>n.a.</td>
</tr>
<tr>
<td>Mg</td>
<td>%</td>
<td>ICP (3)</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>Ti</td>
<td>%</td>
<td>ICP</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Na</td>
<td>%</td>
<td>ICP</td>
<td>0.08</td>
<td>0.01</td>
</tr>
<tr>
<td>Pb</td>
<td>ppm</td>
<td>ICP</td>
<td>105</td>
<td>23</td>
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<tr>
<td>Cu</td>
<td>ppm</td>
<td>ICP</td>
<td>14</td>
<td>32</td>
</tr>
<tr>
<td>Mn</td>
<td>ppm</td>
<td>ICP</td>
<td>123</td>
<td>3</td>
</tr>
<tr>
<td>Th</td>
<td>ppm</td>
<td>ICP</td>
<td>1060</td>
<td>2</td>
</tr>
<tr>
<td>U</td>
<td>ppm</td>
<td>ICP</td>
<td>31</td>
<td>5</td>
</tr>
<tr>
<td>La</td>
<td>ppm</td>
<td>ICP</td>
<td>290</td>
<td>2</td>
</tr>
<tr>
<td>Sr</td>
<td>ppm</td>
<td>ICP</td>
<td>267</td>
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<tr>
<td>Ba</td>
<td>ppm</td>
<td>ICP</td>
<td>188</td>
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<td>6</td>
</tr>
<tr>
<td>Zn</td>
<td>ppm</td>
<td>ICP</td>
<td>11</td>
<td>17</td>
</tr>
</tbody>
</table>

Notes: (1) UBC, Department of Mining and Mineral Process Engineering, Analytical Laboratory (2) GEOSOL, Belo Horizonte, Brazil (3) ICP ionic coupled plasma, ACME Anal.Lab.Ltd., Vanc. (*) ies = ion selective electrode (**) n.a. = not available. (***)Xray flu. = Xray fluorescence.
for the flocculation and adsorption testwork. Part of the -38 micron fraction of the fluorapatite sample was subjected to further sizing by beaker decantation to yield a -6 micron material used for part of the flocculation test programme. The material not settled after 12 hours, was kept for microelectrophoresis. The other mineral samples, either natural or synthetic were used as received.

In no circumstance, were any of the samples subjected to any type of chemical pre-treatment. This option was taken because of many factors, among them:

(i) - the purity of the two natural mineral samples was considered high enough for the purpose of this work, therefore the use of chemical treatment would not improve substantially the grade of the pure minerals.

(ii) - the removal of the low level of impurities present in both samples via a chemical treatment would probably introduce more impurities or would modify the samples in a way that such a treatment can not be justified.
(iii) - the other samples were either chemically pure (for the synthetic ones) or were employed in such a way that the characterization performed and described in Appendix I was considered enough.

(iv) - the use of any type of chemical treatment is, at best debatable. This is especially true for semi-soluble minerals such as apatite. For example, preferential dissolution of some of the lattice constituents during chemical treatment may alter the behaviour of this type of mineral.

5.2 - Chemicals

Table 5.II lists all chemical reagents used in the present work. The same table also gives their uses and a few important remarks, when needed. They include simple inorganic chemicals for pH regulation, ionic strength control and as sources of ionic species. All reagents in this category are of high purity.

Dispersants include members of the "polyphosphate" family and sodium silicates. Na tetraborate was also tested as a dispersant. In this category both chemically pure and commercial grade reagents were used.
<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>FORMULA (M.W.)</th>
<th>SUPPLIER (Grade)</th>
<th>USES</th>
<th>REMARKS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>NaCl (58.44)</td>
<td>Fisher (A.C.S.certified)</td>
<td>Supporting electrolyte</td>
<td></td>
</tr>
<tr>
<td>Chloride</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potassium</td>
<td>KCl (74.56)</td>
<td>Fisher (A.C.S.cert.)</td>
<td>Supporting electrolyte</td>
<td></td>
</tr>
<tr>
<td>Chloride</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potassium</td>
<td>KNO₃ (101.11)</td>
<td>Fisher (A.C.S.cert.)</td>
<td>Supporting electrolyte</td>
<td></td>
</tr>
<tr>
<td>Nitrate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium</td>
<td>NaOH (40.00)</td>
<td>Amachem (Reag.Grade)</td>
<td>pH modifier</td>
<td>preferred on the alkaline gelatinization of starch</td>
</tr>
<tr>
<td>Hydroxide</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potassium</td>
<td>KOH (56.11)</td>
<td>Amachem (Reag.Grade)</td>
<td>pH modifier</td>
<td></td>
</tr>
<tr>
<td>Hydroxide</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonium</td>
<td>NH₄OH (35.05)</td>
<td>Allied Chemical (A.C.S.cert.)</td>
<td>pH modifier</td>
<td>NH₃ content 28 - 30%</td>
</tr>
<tr>
<td>Hydroxide</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrochloric</td>
<td>HCl (36.46)</td>
<td>Amachem (Reag.Grade)</td>
<td>pH modifier</td>
<td></td>
</tr>
<tr>
<td>Acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphuric</td>
<td>H₂SO₄ (98.08)</td>
<td>Amachem (Reag.Grade)</td>
<td>Colorimetric analysis of starch</td>
<td>may also be used as pH modifier</td>
</tr>
<tr>
<td>Acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitric</td>
<td>HNO₃ (63.01)</td>
<td>Allied Chemical (A.C.S.cert.)</td>
<td>Cleaning of glassware</td>
<td>Used in the HNO₃/ethanol cleaning process</td>
</tr>
<tr>
<td>Acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium</td>
<td>CaCl₂.2H₂O (147.02)</td>
<td>Fisher (A.C.S.cert.)</td>
<td>Source of Ca aqueous dihydrate</td>
<td></td>
</tr>
<tr>
<td>Chloride</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnesium</td>
<td>MgCl₂.6H₂O (203.31)</td>
<td>Baker (A.C.S.cert.)</td>
<td>Source of Mg aqueous 6-hydrate</td>
<td></td>
</tr>
<tr>
<td>Chloride</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COMPOUND</td>
<td>FORMULA (M.W.)</td>
<td>SUPPLIER (GRADE)</td>
<td>USES</td>
<td>REMARKS</td>
</tr>
<tr>
<td>---------------------</td>
<td>----------------</td>
<td>------------------</td>
<td>-----------------------------</td>
<td>------------------------------</td>
</tr>
<tr>
<td>Aluminum Chloride</td>
<td>AlCl₃·6H₂O</td>
<td>Baker (A.C.S.cert.)</td>
<td>Source of Al aqueous species</td>
<td>6 - hydrate</td>
</tr>
<tr>
<td>Sodium Pyrophosphate</td>
<td>Na₄P₂O₇·10H₂O</td>
<td>Fisher</td>
<td>dispersant</td>
<td>decahydrate</td>
</tr>
<tr>
<td>Sodium Tetraborate</td>
<td>Na₂B₄O₇</td>
<td>B.D.H. (purified)</td>
<td>dispersant</td>
<td>-</td>
</tr>
<tr>
<td>Sodium Hexametaphosphate</td>
<td>(NaPO₃)₆</td>
<td>Fisher (purified)</td>
<td>dispersant</td>
<td>65 - 68%P₂O₅</td>
</tr>
<tr>
<td>Sodium Tripolyphosphate</td>
<td>Na₅P₃O₁₀</td>
<td>Staufer (technical)</td>
<td>dispersant</td>
<td>85%</td>
</tr>
<tr>
<td>Sodium Metasilicate</td>
<td>Na₂SiO₃·5H₂O</td>
<td>Fisher (technical)</td>
<td>dispersant</td>
<td>-</td>
</tr>
<tr>
<td>METSO 1048</td>
<td>51% Na₂O, 47% SiO₂</td>
<td>National Silicates Ltd. (commercial)</td>
<td>sodium silicate with Na₂O : SiO₂ = 1:1</td>
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</tr>
<tr>
<td>METSO 200</td>
<td>60.8%Na₂O, 28.8%SiO₂</td>
<td>National Silicates Ltd. (commercial)</td>
<td>sodium orthosilicate with Na₂O : SiO₂ = 2:1</td>
<td></td>
</tr>
<tr>
<td>METSO 99</td>
<td>36.7%Na₂O, 38.1%SiO₂</td>
<td>National Silicates Ltd. (commercial)</td>
<td>hydrated Na₃sesquisilicate with Na₂O : SiO₂ = 3:2</td>
<td></td>
</tr>
<tr>
<td>EDTA</td>
<td>Na₂C₁₀H₁₄O₈N₂·2H₂O (372.08)</td>
<td>Fisher (A.C.S.cert.)</td>
<td>dispersant</td>
<td>disodium ethylenediaminetetraacetate</td>
</tr>
<tr>
<td>Corn Starch</td>
<td>(C₆H₁₀O₅)ₙ</td>
<td>Fisher (U.S.P.)</td>
<td>flocculant</td>
<td>-</td>
</tr>
<tr>
<td>Potato Starch</td>
<td>(C₆H₁₀O₅)ₙ</td>
<td>Fisher (purified)</td>
<td>flocculant</td>
<td>-</td>
</tr>
<tr>
<td>Starch</td>
<td>(C₆H₁₀O₅)ₙ</td>
<td>(U.S.P.)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>COMPOUND</td>
<td>FORMULA (M.W.)</td>
<td>Supplier (Grade)</td>
<td>Uses</td>
<td>Remarks</td>
</tr>
<tr>
<td>--------------</td>
<td>----------------</td>
<td>------------------</td>
<td>------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>Tapioca</td>
<td>(C₆H₁₀O₅)ₙ</td>
<td>- (commercial)</td>
<td>flocculant</td>
<td>from Thailand</td>
</tr>
<tr>
<td>Starch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Collamill</td>
<td>(C₆H₁₀O₅)ₙ</td>
<td>Refinações de Milho Brasil (commercial)</td>
<td>flocculant</td>
<td>a non modified corn starch</td>
</tr>
<tr>
<td>Dextran</td>
<td>(C₆H₁₀O₅)ₙ</td>
<td>BDH (90%)</td>
<td>flocculant</td>
<td>a bacterial polysaccharide</td>
</tr>
<tr>
<td>grade A</td>
<td>(200.000 - 275.000)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amilose</td>
<td>(C₆H₁₀O₅)ₙ</td>
<td>BDH (purified)</td>
<td>flocculant</td>
<td>from potato starch</td>
</tr>
<tr>
<td>Amylopectin</td>
<td>(C₆H₁₀O₅)ₙ</td>
<td>BDH (purified)</td>
<td>flocculant</td>
<td>from potato starch</td>
</tr>
<tr>
<td>D-glucose</td>
<td>C₆H₁₀O₅.H₂O (180.167)</td>
<td>BDH (Reag.Grade)</td>
<td>monomer of -</td>
<td></td>
</tr>
<tr>
<td>(dextrose)</td>
<td></td>
<td></td>
<td>flocculants</td>
<td></td>
</tr>
<tr>
<td>Sodium</td>
<td>CH₃(CH₂)₇CH CH(CH₂)₇ -COO Na (304)</td>
<td>Fisher (purified)</td>
<td>collector</td>
<td></td>
</tr>
<tr>
<td>Oleate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dodecylamine</td>
<td>C₁₂H₂₅NH₃Cl (221.82)</td>
<td>Eastman Koday Co.</td>
<td>collector</td>
<td></td>
</tr>
<tr>
<td>Hydrochloride</td>
<td>(pure)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>CCl₄</td>
<td>Fisher</td>
<td>for I.R.testwork</td>
<td></td>
</tr>
<tr>
<td>Tetrachloride</td>
<td>(153.82)</td>
<td>(spectralanalized)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potassium</td>
<td>KBr</td>
<td>Fisher (I.R.grade)</td>
<td>for I.R.testwork,</td>
<td></td>
</tr>
<tr>
<td>Bromide</td>
<td>(119.01)</td>
<td></td>
<td>preparation of pellets</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>C₆H₅OH (94.11)</td>
<td>MCB Chemicals</td>
<td>colorimetric analysis</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(A.C.S.cert.)</td>
<td></td>
<td>of starch</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>CH₃OH (36.07)</td>
<td>Fisher (A.C.S.cert.)</td>
<td>cleaning of glassware see HNO₃ remark</td>
<td></td>
</tr>
<tr>
<td>COMPOUND</td>
<td>FORMULA (M.W.)</td>
<td>Supplier (Grade)</td>
<td>Uses</td>
<td>Remarks</td>
</tr>
<tr>
<td>----------</td>
<td>---------------</td>
<td>-----------------</td>
<td>------</td>
<td>---------</td>
</tr>
<tr>
<td>Butanol</td>
<td>CH$_3$(CH$_2$)$_3$OH (74.12)</td>
<td>Amachem (Reag.Grade)</td>
<td>fractionation of starch</td>
<td>-</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH$_3$CH$_2$OH (50.07)</td>
<td>Fisher (A.C.S.cert.)</td>
<td>extraction of fats from starch</td>
<td>-</td>
</tr>
<tr>
<td>Iodine</td>
<td>I (At.Wt.126.90)</td>
<td>Fisher (A.C.S.cert.)</td>
<td>iodometric analyses of starch</td>
<td>-</td>
</tr>
<tr>
<td>Potassium</td>
<td>KI</td>
<td>Fisher (A.C.S.cert.)</td>
<td>as above</td>
<td>-</td>
</tr>
<tr>
<td>Iodine</td>
<td>(166.01)</td>
<td>Fisher (A.C.S.cert.)</td>
<td>pH meter standardization</td>
<td>pH 4.01, 7.41 and 10.41</td>
</tr>
</tbody>
</table>
The polymers used in the present work include only polysaccharides with monomer α-D-Glucose. Most of them are reagents and a few are reagent grade. They were characterized in this work by various methods such as viscometry, light scattering and infrared spectroscopy (see section 6.2).

Only two surfactants were selected as collectors for apatite. They represent two major types of collectors used in the beneficiation of phosphate ores.

The other chemicals listed in table 5.II were used for a variety of purposes, including for instance analysis of starches, cleaning of glassware and preparation of standards.

5.3 - Equipment and Techniques

5.3.1 - Sizing

Three different sizing procedures were used. Coarser particles ( >38 micron) were sized by screening. A "Ro Tap" screen shaker was used for dry screening and a single screen vibrator (for standard 8" screens) was used for wet screening. Sieves were periodically cleaned in an ultrasonic bath.

Conventional beaker decantation was used for the splitting of size fractions below 38 micron. Stokes law behaviour was assumed in these cases.
Size analyses for sub-sieve size fractions were performed in Elzone Celloscope (Particle Data Inc.). In the Elzone instrument, an aqueous suspension of less than 1% solids (by wt.) of particles to be analyzed is kept from settling by constant agitation. An inorganic dispersant such as Na-hexametaphosphate was used. The aqueous suspension is prepared with an electrolyte, and has a constant resistivity. A tube with a calibrated orifice is submerged in the suspension container. Both tube and container have electrodes, and an electrical circuit is created between them. Vacuum is applied to the tube and the suspension is drawn through the orifice, causing a momentary resistance change ($\Delta R$). The change in resistance is related to the particle volume as follows:

$$\Delta R = \frac{\rho_o v A^2}{A^2} \left( \frac{i}{1 - \rho / \rho_o} \right)^{-1}$$

(EQ. 5.3.1)

where:

- $\rho_o$ = electrolyte resistivity
- $v$ = particle volume (effective)
- $A$ = orifice area normal to the axis of the tube
- $\rho$ = effective particle resistivity
- $a$ = cross sectional area of particle

Each particle passage produces a voltage pulse of magnitude proportional to the particle volume. The resultant series of pulses is electronically scaled and counted.
These data are then manipulated by a mini-computer. Outputs can be either in the form of a histogram of volume distribution versus log size or cumulative per thousand distribution above size versus size. A log-normal distribution is assumed. Log mean, mode and median are also calculated automatically. Details on the operation and principles of the Elzone size analyser are found in anon. (1977).

5.3.2 - Surface Area Determination

Surface areas of mineral samples were estimated by applying a multipoint BET technique. Nitrogen and Helium were used as adsorbate and carrier gases, respectively. A Quantasorb (Quantachrome Corporation) BET unit was employed. The technique is standard for measuring surface area of powders. Details can be found elsewhere (for operational details see anon., 1970; for BET theory and applications in the determination of surface see for example Hiemenz, 1977 - pp.322-335 and Leja, 1982 - pp. 379-381).

5.3.3 - Spectroscopic Techniques

5.3.3.1 - Infrared Spectroscopy

Infrared spectra of minerals and chemicals were recorded on a Perkin Elmer 283-B double beam, optical null
A spectrophotometer. Wavelength calibration of the spectrophotometer was checked by examining a standard polystyrene film, the spectral band positions of which are accurately known. The spectral range of the unit is from 4000 to 200 cm\(^{-1}\) (wavenumbers).

The KBr pellet method was used in all cases. A mixture of approximately 1 mg of sample (finely ground and oven dried for 24 hours at 80-100°C) and 300 mg of KBr powder (infrared grade) was transferred to a die (Perkin Elmer model 186-00251), evacuated for 2 to 5 minutes and then pressed at approximately 300 kPa for 1 minute.

A Perkin Elmer Infrared Data Station is connected to the spectrophotometer. It is capable of performing different tasks such as mathematical smoothing, flattening, peak position determination and expansion of recorded spectra, which are saved on disc for further treatment and analysis. The same data station unit is also capable of controlling the spectrophotometer's plotter.

5.3.3.2 - U.V - Visible Spectroscopy

Two U.V. - Visible spectrophotometers were used in the present work: (i) Perkin Elmer model Lambda 3 and (ii) Baush and Lomb Spectronic 21. The first unit has a double beam design and is capable of recording U.V. - Visible spectra liquid samples (5ml optical cells with 1.0 cm of path length) from 900 to 180 nm. It can either plot the complete
spectrum for a given wavelength range or it can make measurements at a pre-established wavelength. The type of output and scanning can be selected (e.g. % transmittance, absorbance or "concentration" are the types of outputs available). This unit was used to obtain the spectra of starches after their reaction with iodine. It was also used in the study of the interaction between starches and surfactants.

The second unit (Spectronic 21) is a single beam spectrophotometer, equipped with 5ml cylindrical glass cuvettes. It was used for most of the quantitative work in the determination of starch concentrations with the iodine method. The readings of this unit are in the form of % transmittance at a pre-set wavelength. To adjust the transmittance reading, a black coloured cylinder of the same diameter of the cuvettes is used to give zero % transmittance, this operation being repeated every time the unit is turned on. The precision of the readings is 0.5% transmittance units. After obtaining the transmittance data they were converted to absorbance. It was also used for qualitative dispersion testwork, where the % transmittance of a suspension to light of a wavelength of 450 nm after a determined settling period was used as an indication of the stability of such a suspension.
5.3.3.3 - Light Scattering

The molecular weight of a polymer can be determined from the ratios of the intensity of scattered light (measured at right angles to the incident beam) to the intensity of the transmitted beam as determined for solutions of several different concentrations. This ratio can be measured using a light scattering photometer. In the present work a Brice-Phoenix Universal Light Scattering Photometer was used. It comprises, briefly, a light source, a set of filters and collimators, a turntable where the sample is positioned, a photomultiplier tube and a light trap. A more detailed description can be found in Hiemenz (1977) - pp.175-178.

Theory:

If polarized light of intensity \( I_0 \) is passed through a macromolecular solution, each molecule scatters the light in all directions and becomes effectively a source of light of the same wavelength as the incident beam. The ratio of intensity of the scattered beam - \( i_s \) - (measured at an angle \( \theta \) to the incident beam) to \( I_0 \) is defined by the Rayleigh ratio \( R_\theta \) given by:

\[
R_\theta = \frac{i_s r^2}{I_0 \cos^2 \theta} = \frac{16 \pi^4 a^2}{\lambda_o^4}
\]

(EQ.5.3.2)

where:

\( r \) is the distance of the observer from the scattering centre.
\[ a \text{ is a constant (the polarizability of the particle)} \]
\[ \lambda_0 \text{ is the wavelength of the light.} \]

It can be shown (Hiemenz, 1977) that since \( n^2 - n_0^2 = 4 \pi N a \)

then

\[ R_\theta = \frac{4 \pi^2 n_0^2 (dn/dc)^2 M c}{N \lambda_0^4} \]  

(EQ. 5.3.3)

where:

\( dn/dc \) is the refractive index gradient with respect to concentration

\( c \) is concentration in g/ml

\( M \) is the molecular weight of the macromolecule

\( N \) is Avogadro's number

\( n \) is the refractive index of the solution

\( n_0 \) is the refractive index of the solvent

This equation assumes an infinitely dilute ideal solution.

For real solutions a correction must be applied as follows:

\[ R_\theta = \frac{4 \pi^2 n_0^2 (dn/dc)^2 c}{N \lambda_0^4 (1/M + B^* c)} \]  

(EQ. 5.3.4)

where

\( B^* = 2B \) is the second virial coefficient.
Application:

With the turntable set at 90° the photomultiplier tube measures only scattered light. With the disc of the turntable at 0° the photomultiplier tube measures the transmitted light. The intensity of the scattered light is several orders of magnitude less than the transmitted beam and in practice it is not feasible to measure such a wide range with a single photomultiplier tube. Thus the transmitted beam is attenuated with neutral density filters of known transmittance and a calibrated working standard filter which is in position only when this beam is being measured.

The Rayleigh ratio \( R_{90} \) when \( \theta = 90° \) is given by:

\[
R_{90} = \left( \frac{TD}{\pi (1.049) h} \right) n^2 \left( \frac{F G_s}{G_w} \right) \tag{EQ. 5.3.5'}
\]

where:

- TD is the diffuse transmittance of the working standard filter.
- h is the width of the diaphragm.
- F is the product of the transmittance of the filters used in the determining the scatter ratio.
- \( G_s \) is the meter reading on the scattered light measured at 90° to the incident beam.
- \( G_w \) is the meter reading on the transmitted light measured directly into the incident beam.
n is the refractive index of the solution.

\( R_{g0} \) for the solute is determined by subtracting \( R_{g0} \) for the solvent from \( R_{g0} \) for the solution. The molecular weight is determined from a plot of \( H'c/R_{g0} \) (solute) versus the solute concentration, \( c \), in g/ml since from EQ. 5.3.4:

\[
\frac{H'c}{R_{g0}} = \frac{1}{M} + 2Bc
\]  

(EQ. 5.3.5)

where:

\[
H' = \left( \frac{2 \pi 2 n^2 n_0^2 (n-n_0/c)^2}{\lambda_0^4 N} \right)
\]  

(EQ. 5.3.6)

The application of this last equation to the determination of molecular weights of the starch samples used in this work is discussed later in this thesis (see section 6.2.4).

5.3.4 - Electrophoresis and Related Experiments

Electrophoretic mobility was determined with a Zeta Meter (Zeta Meter Inc., New York). A cylindrical lucite cell, type II U.V.A. (No. S2346), size 0.0, with a constant \( K=69 \), was used. It has an interelectrode distance of 10cm. A Pt cathode (flat) and Pt or Mo anodes (round), standard for the Zeta Meter, were utilized, depending on the conductivity of the sample.
Temperature of the sample suspensions was maintained, in most cases, at 23±0.5°C with a water bath. The electrophoretic cell was flushed with distilled water at 23.5°C before the test suspension was added. The expected temperature rise is 1.5°C during electrophoresis, thus the final test temperature was approximately 25°C (Zeta Meter Manual, Zeta Meter Inc., 1975).

Finely divided, pure mineral samples in very dilute aqueous suspensions were subjected to electrophoresis. An average of at least 20 measurements were made in each test run, and the mean and standard deviation of the electrophoretic mobilities of the particles were computed. Only the results showing a standard deviation from the mean of less than or equal to 0.35 were accepted. Electrophoretic mobility/pH curves were obtained under three different conditions, for the mineral samples:

(i) - in distilled water,
(ii) - in the presence of an indifferent electrolyte,
(iii) - in the presence of specifically adsorbing ions.

The starch samples were also subjected to electrophoresis in order to verify the presence of ionic groups. These experiments were conducted only at one pH value, of 5.5 to 6.0.

The point of zero charge of the fluorapatite sample
was determined by applying the Mular and Roberts (1966) pH technique. One variation of this technique, generally referred to as the Ahmed (1969) method was also used. As previously discussed (see section 4.3.1), for minerals such as apatite, a single value for the point of zero charge (pzc) must be accompanied by the conditions of the experiment, since one can define a line of zero charge for the mineral depending on the concentration of the different potential determining ions. The value of zero electrophoretic mobility (isoelectric point or iep) is that determined by applying the electrophoretic technique described above. Presentation of the results obtained for the minerals is given in section 6.1.3, for starches in section 6.2.2.

5.3.5 - Viscometry

In contrast to starch paste viscosity, in which a rheological property is the main objective, the measurement of intrinsic viscosity of dilute solutions of starches is performed to obtain information regarding flow properties. These flow properties for dilute solutions (less than 0.5% by weight) are measured under such conditions that the polymolecules are as free as possible of entanglements. The intrinsic viscosity (or the limiting viscosity number, according to IUPAC nomenclature) is generally related to molecular weight by the Mark-Houwink equation as follows (Greenwood, 1964; Seymour and Carraher, 1981):
\[ |\eta| = KM^a \]  

(EQ.5.3.7)

where:

- \( |\eta| \): limiting viscosity number (ml/g)
- \( M \): average molecular weight
- \( K \): empirical constant for a given polymer solvent system, and
- \( a \): empirical exponent that is a function of the shape of the polymer coil in solution.

Furthermore:

\[ |\eta| = \lim_{c \to 0} \left( \frac{\eta_{sp}}{c} \right) \]  

(EQ.5.3.8)

where:

- \( c \): grammes of polymer per 100 ml of solution
- \( \eta_{sp} = \frac{\eta - \eta_0}{\eta_0} \) in which \( \eta_{sp} \) is the specific viscosity
- \( \eta \): is the viscosity of the solution and \( \eta_0 \) is the viscosity of the solvent.

An Ostwald-type capillary viscometer was used for the determination of limiting viscosity numbers of potato amylose solutions. Although absolute values of average molecular weight can not be obtained by viscosity methods without calibration by an independent measurement, the knowledge of the limiting viscosity number and the use of
tabulated constants for the system can provide some information on the molecular size of the sample used in the present investigation. Details on the technique to measure limiting viscosity number for starches are given by Greenwood (1964), Danishefsky et al. (1970), and Seymour and Carraher (1981). The results and discussions are presented in section 6.2.3.

The capillary viscometer was calibrated with distilled water and benzene (A.C.S. cert.). Each flow time measurement was performed at least 3 times. The average flow time was used in the calculations. Temperature did not vary more than 0.5°C.

5.3.6 - Conductivity Testwork

The specific conductivity or conductance of a solution can be defined as the reciprocal resistance across two non-polarized electrodes which form the opposite sides of a cube of 1 x 1 x 1 cm. Electrolytic solutions can conduct electrical current through the movement of ions, belonging to the category of conductors of the second class (Crockford and Knight, 1964).

When two electrolytes are added, the net conductance is the sum of the individual contributions by the ions present in both of them. Thus when two electrolytes BA and CD are added, the net conductance is given by:
the sum of the mobilities of all ions. However, if there is ion-ion interaction, the above relationship does not hold and the net conductance depends upon the solubility of the new species as well as the mobility of its ions (Khosla, 1983). Therefore, upon adding two electrolytes, if the conductance can not be explained by mobilities of the ions known to be present in the two electrolytes, an ion-ion interaction or complex formation is indicated.

In the present testwork, known solutions of starch at different concentrations were added to calcium chloride solutions also of known concentration, at pre-established pH values. The conductance of these solutions, alone and in combination, was measured with a Radiometer Conductivity Meter, Type CDN2d, equipped with a conductivity cell type CDC 104. This cell has three electrodes in the form of a platinum sheet placed around a glass tube and enclosed in a glass jacket (anon., Radiometer Instruction Manual, 2nd ed.). The top and bottom rings are connected and grounded to the chassis through the shield of the coaxial cable while the centre ring is connected to the centre conductor of the cable. This arrangement which is a special feature of the conductivity cell, provides an effective electrical shielding of the flows of currents between the electrodes thus enabling the cell to be used for measurements in grounded vessels.
When using this cell, all three rings must be covered with the test solution, and care should be taken to avoid the formation of air bubbles inside the walls of the cell. The cell is equipped with small holes where the bubbles can escape. The cell constant is 1.0 cm.

The Radiometer Conductivity Meter has two measuring ranges: 0-500 micromho and 0-500 millimho. It also has two measuring frequencies: 70 Hz for conductance below 150 micromho and 3000 Hz for conductance values above 150 micromho. The measuring accuracy is 2% of full scale deflection. The step-by-step operation of this unit is given in the Instruction Manual (see reference above).

5.3.7 - Qualitative Dispersion Testwork

In a preliminary phase, a series of qualitative dispersion experiments was performed in order to characterize the effect of different chemicals on the degree of stability of mineral suspensions. These tests were performed on three of the mineral samples used in this work: fluorapatite from Monteiro, quartz and kaolinite. For this purpose, the % transmittance of the mineral suspension being tested was measured at 450 nm after a pre-established settling period. The Baush and Lomb U.V. - Visible spectrophotometer Spectronic 21, previously described, was used. The results obtained should be regarded as a relative measure of the degree of dispersion/aggregation of the suspensions but
should not be compared among the three minerals due to their size and specific gravity differences. The results and discussions are presented in section 6.1.4.

5.3.8 - Adsorption Testwork

To investigate the adsorption of starches on the mineral samples used in the present work, both a qualitative, preliminary adsorption test programme and a more comprehensive quantitative test programme were performed. In the first case, with the help of colour photography, the adsorption of starches on apatite and silica was followed at one arbitrarily set condition (25ppm of polymer and pH of approximately 10). During these tests, an equal amount of I/KI was added to test tubes containing both mineral powder and starch and starch only. The tubes were set side by side in a test tube rack and colour pictures were taken, after a period of approximately 24 hours. These photographs were able to show the preferential adsorption of all starches tested on the apatite surface as compared to the silica surface. The colour imparted to the starch solutions by the addition of iodine was transferred to the mineral, whenever starch was extensively adsorbed. In the case of no adsorption or low affinity for the surface, the colour of the powder (silica) remained unchanged, and the supernatants containing starch stayed strongly coloured. A NIKON 35mm camera, equipped with a tripod and standard 200ASA KODAK VR
film, was used. Two flood lights (500 watts each) were set at a 45° angle in relation to the front of the test tube rack.

In the second series of adsorption tests, the amount of starch adsorbed onto the surfaces of fluorapatite and quartz was measured. The following experimental procedure was used:

(i) - a pre-weighed amount of mineral powder was transferred to cylindrical glass vials of about 75ml capacity, equipped with plastic lids.

(ii) - fifty ml of the starch solution to be tested, at the pre-chosen (initial) concentration and pH was also added to the vial containing the mineral.

(iii) - the vial was covered with the lid and hand shaken by turning it end over end 5 times.

(iv) - a set of vials, enough to obtain a complete adsorption isotherm was then transferred to a shaker (Environ Orbit Laboratory Shaker). The shaking speed was 300 rpm and the shaking time for most of the tests was 60 minutes (different only for the adsorption kinetics tests).

(v) - After the shaking period was completed, the vials were removed from the shaker. Great care was taken not to disturb the settled
phase in the case of flocculation. In some tests, the supernatant was removed for Ca analysis and % transmittance measurements (complementary tests). In most cases (adsorption test) the supernatant was filtered through a glass fiber Whatman A934 paper, in a conventional vacuum filtration set up. The final pH was then measured.

(vi) - the filtrate was then analysed for residual starch concentration by the colorimetric $I_2/KI$ technique. Care was taken to adjust the final pH of the filtrate to a known value.

(vii) - the amount of starch adsorbed was then calculated by difference (i.e. the amount adsorbed was considered to be equal to the initial concentration minus the residual concentration; adsorption onto the glass vial walls was considered to be extremely small).

In some tests, a solution containing Ca ions at a previously selected concentration was also used in order to investigate the effect of these ions in the adsorption behaviour of starches on the minerals studied.

Before performing the adsorption test programme, an extensive investigation of the analytical method chosen for the determination of residual starch concentrations was
performed (see section 6.4.2). The effect of shaking under similar conditions of the adsorption tests and of filtration were thoroughly investigated, before the final selection of this colorimetric technique. The Baush and Lomb U.V. - visible spectrophotometer Spectronic 21 was used for the determination of the residual concentrations and calibration curves for starch solutions reacted with iodine.

5.3.9 - Single Mineral Flocculation Testwork

Although there are many different ways to perform this type of experiment, some of them, such as refiltration rate, settled volume, height of settled bed, and height of consolidated filter cake give only very specialized information (see for example Slater and Kitchener, 1966, for details). For this reason, the techniques selected in the present work are "gravitic" methods where either a degree of flocculation or a zone settling rate can be directly derived. Some complementary tests were performed using the same technique described earlier for the qualitative dispersion test programme.

The first of the two "gravitic" techniques used a plexiglass tube with two outlets, as shown in figure 5.1. The type of outlets were designed to avoid suction of material below the set height, which could modify the final results because of the small volume of sample used in each test. The tube was "calibrated" with distilled water. After
Figure 5.1 - Schematic View of Tube Used for Preliminary Dispersion/Flocculation Tests.
removing 20 consecutive 10ml increments, the average value was 10.1 ±0.5ml. The other important dimensions of the tube are given in figure 5.1. A series of trial tests was performed to develop a reproducible procedure with the kaolinite sample. The results obtained with the tube were checked against a more conventional technique also used for the same purposes—the Andreasen pipette (see Sadowski and Laskowski, 1980). For the kaolinite sample they were almost identical (de Araujo and Galery, 1987). The procedure used can be summarized as follows:

(i) - 30ml of a suspension containing 0.5% solids by wt. of the mineral being tested is transferred to the tube (there is a 30ml mark on the tube wall.

(ii) - the desired reagents are added to the tube.

(iii) - the tube is stoppered and inverted 5 times.

(iv) - after a pre-established period of time (1,2 or 5 minutes for example), one of the two outlets is opened and 10ml (for the upper outlet) or 20ml (for the bottom outlet) of suspension is removed. For the majority of tests performed in the present work, the upper outlet was the one chosen.

(v) - the sample removed is dried and carefully weighed.

(vi) - a % degree of flocculation is calculated by
the formula:

\[ F_{h,t} = 100 - \left[ 100 \frac{W_{o}}{W_{i}} \right] \]  

(EQ.5.3.10)

where:

- \( F_{h,t} \) is the degree of flocculation expressed in %;
- \( W_{o} \) is the wt. in grams of outlet sample (10 or 20 ml);
- \( W_{i} \) is the wt. in grams per 10 or 20 ml of original suspension.

The degree of flocculation calculated by EQ.5.3.10 is only relative. However, for a set of experiments performed under similar conditions, it can be used as a relative measurement of the state of stability of the suspension. Most of the tests were capable of selecting the starting conditions for the more extensive testing performed by the technique described next.

The second "gravitic" technique used is a variation of the conventional graduated cylinder tests used for thickener design (discussed for instance by Pearse, 1980 and 1982). The basic differences are the size of the graduated cylinder selected and the measurement only of the linear portion of the settling curve. It has been used by Iwasaki and co-workers (1980 and 1983) to evaluate flocculation. It consists basically of measuring the settling of a suspension in a 100ml graduated cylinder, following only the first
minutes or seconds of zone settling. From the slope of this settling curve (linear portion) a zone settling rate in appropriate units is calculated (e.g. cm/minute). In this test programme a regression analysis of each settling data set was performed. Therefore the zone settling rate reported represents the best straight line obtainable. Very high correlation coefficients were obtained in most of the cases. A few 1000ml graduated cylinder tests were performed to compare the order of magnitude of the settling rates obtained with two sizes of sedimentation vessels. These seem to indicate that both techniques give comparable results for the solid concentration chosen (40 g per litre, i.e. 3.9 solids by wt.)

5.3.10 - Microflotation Testwork

In order to investigate the effect of starches on the cationic and anionic flotation of apatite, microflotation tests in a modified Hallimond tube were performed. The tube is only slightly different from the one described by Fuerstenau et al. (1957). Medical air was used as the gas source, at a flow rate of approximately 40 cm³ per minute. The magnetic stirrer was always set to the same level. Flotation time was also set constant at 1 minute, except for a few experiments in which the knowledge of kinetic parameters was judged important. Each test used approximately 1 gram of mineral in the size fraction between
212 and 150 microns. The mineral samples used were fluorapatite from Monteiro, apatite from Itataia and quartz from Ottawa. The % floated in 1 minute (called "recovery" by many authors and "floatability" or "hydrophobicity" by others) was calculated from the mass balance in the case of single mineral tests and from the ingredient balance in the few cases where a mixture of two minerals (fluorapatite and quartz) was employed. The results obtained for the collector systems are presented and discussed in section 6.6.

5.3.11 - Miscellaneous

5.3.11.1 - Mixing and Shaking

Both mechanical and magnetic stirrers were used to prepare solutions and to condition minerals with reagents. They include the T-Line Laboratory stirrer (mechanical) and Corning hot plate-magnetic stirrer model PC 351. Both have adjustable stirring velocities.

Shaking of samples for adsorption testwork was done in a Lab-Line Orbit Environ-Shaker (Lab-Line Instruments), with controlled temperature (20 to 50°C) and speed (up to 500 rpm). Whenever hand shaking is referred to in this thesis, the procedure used is described.
5.3.11.2 - pH Measurement

A Fisher Accumet 230 pH/ion meter was used for pH measurements. Combination glass electrodes (Beckman) were standardized daily against buffer solutions of pH 4.01 and 10.4 (see table 5.II for details on the buffers). In general, the pH of a test run is the average pH, i.e. the arithmetic mean obtained from initial and final pH values. In some cases only final or initial pH values were obtained. In these cases the test pH is identified as initial or final by the subscripts "i" or "f".

5.3.11.3 - Filtration and Drying

In most cases, filtration was performed in a standard laboratory vacuum filtration apparatus. Buchner filters with Whatman 934 AH glass fiber filter paper were used. In a few cases, a micropore filter apparatus was used, with standard filter paper of 5 and 1 micron.

Drying was accomplished in laboratory ovens with controlled temperature. In most cases drying of samples was performed overnight at temperatures always below 100°C. Care was taken to avoid any type of contamination during drying. Whenever necessary aluminum foil was used to cover material inside the ovens.
5.3.11.4 - Centrifugation

An IEC International Centrifuge capable of speeds up to 20,000 rpm was used. The main application was in the clarification of solutions and suspensions before analyses.

5.3.11.5 - Weighing

A Mettler analytical balance model H 20 T (160 g maximum charge) was used for high precision weighing. Two other Mettler balance models Pc440 (400 g maximum charge) and P 5 N (4 kg maximum charge) were used for less precise work (1/100 and 1/10g readings, respectively).

5.3.11.6 - Time Measurement

A Timex stopwatch with digital readings was used for most of the work. The precision of the readings is 1/100 of a second. Some pieces of equipment utilized in this work have their own time measuring devices, and in such cases, no external calibration was performed.

5.3.11.7 - Microscopy

Both optical and electron microscopy were applied. An ETEC Autoscan scanning electron microscope, equipped with an X-ray energy dispersive spectrophotometer, a JEOL
electron microprobe model JXA-3A and different models of binocular microscopes were utilized for performing different tasks.
6 - RESULTS AND DISCUSSIONS

6.1. - Characterization of Mineral Samples

6.1.1 - Infrared Spectroscopy and Other Techniques

In order to characterize fully the mineral specimens used in the present work, they were subjected to a series of tests. Infrared spectroscopy was chosen as the main mineral identification and characterization tool. Especially for apatites, there is an extensive literature available on the subject. In more general terms, the application of infrared spectroscopy to pure minerals has some advantages such as (Estep-Barnes, 1977):

(i) - it is one of the most powerful single techniques available today for mineral analysis.

(ii) - the infrared spectrum of a mineral yields basic information on interatomic bonding and it can serve, in most cases, as a "fingerprint" to give proof of identity without resource to any other analytical method.

(iii) - it needs of only a few milligrammes of sample for a complete spectrum.

Allied to the advantages above, the availability in
the laboratories of the Department of Mining and Mineral Process Engineering (UBC) of a modern infrared spectrophotometer (see section 5.3.3.1 for details), contributed to the selection of infrared spectroscopy as a main characterization tool used for mineral specimens.

As discussed in section 5.1, not all mineral samples were characterized to a same extent. However, for comparison purposes, figure 6.1 presents the infrared spectra of four different apatites, including the one from Monteiro, used for the major part of the testwork done. In figure 6.2, the spectrum of the hydroxyapatite sample is displayed. In the first case, only the portion of the infrared spectrum between wavenumbers of 2000 and 300 cm\(^{-1}\) is presented. For wavenumbers lower than 300 cm\(^{-1}\), the technique used, viz. KBr pellets, is not applicable due to adsorption by the KBr matrix. Also in figure 6.1 the ordinate scale does not give absolute values for the % transmittance because the spectra were modified by computer to be displayed together in one figure. In figure 6.2 the regions of the infrared spectrum shown are the ones where major infrared bands were displayed by the mineral. For completeness, figures 6.3 and 6.4 show the infrared spectra of quartz and kaolinite, respectively. They will be briefly discussed later in this section.

Interpretation of the I.R. Spectra

The infrared spectrum of apatites is dominated by
Figure 6.1 - Infrared Spectra of Apatites.
Figure 6.2 - Infrared Spectrum of Synthetic Hydroxyapatite.
Figure 6.3 - Infrared Spectra of Quartz.
Figure 6.4 - Infrared Spectrum of Kaolinite.
vibrations of PO\textsubscript{4} ionic groups. In its "free" state, PO\textsubscript{4} has a group site symmetry T\textsubscript{d}\textsuperscript{(1)} (i.e. a perfect tetrahedron, space group 43m in the cubic system, having a four-fold rotation inversion axis(4), a three-fold rotation axis(3) and a mirror reflection plane (m)). The selection rules for this space group according to Ross (1974) give an A\textsubscript{1} symmetric stretch (\nu\textsubscript{1}), and E bend (\nu\textsubscript{2}), an F\textsubscript{2} antisymmetric stretch (\nu\textsubscript{3}), and an F\textsubscript{2} bend (\nu\textsubscript{4}). The F\textsubscript{2} modes are both infrared and Raman-active (Figure 6.5).

Although there is some disagreement concerning the assignment for the \nu\textsubscript{2} band position\textsuperscript{(2)}, the following ranges for the P-O fundamental vibration are given by Ross (1974):

\nu\textsubscript{1} 980-930 cm\textsuperscript{-1}
\nu\textsubscript{2} 420 or 360 cm\textsuperscript{-1} (doubly degenerate)
\nu\textsubscript{3} 1080-1010 cm\textsuperscript{-1} (triply degenerate)
\nu\textsubscript{4} 570-515 cm\textsuperscript{-1} (triply degenerate)

Considered isolated and possessing a T\textsubscript{d} group symmetry, all P-O bonds in a PO\textsubscript{4} group would be equivalent.

\textsuperscript{(1)} In molecular spectroscopy, the Schoenflies notation is often used. Crystallographers prefer to use the international notation. The correspondence between the two can be found in Kittel (1956), p.19.

\textsuperscript{(2)} The old literature normally assigns \nu\textsubscript{2} to a Raman band occurring at 360 cm\textsuperscript{-1} (e.g. Vratny et al., 1961). More recent publications assign a higher value to the same vibration, approximately at 420 cm\textsuperscript{-1} (e.g. Nakamoto, 1970).
Figure 6.5 - The PO₄ Group:

(I) Regular Tetrahedron with Symmetry T_d

(II) Distorted Tetrahedron with Symmetry C₃

A, B, C : directions of dipole moments;
σ : symmetry plane;
Phosphorus is at the centre,
Oxygens at the corners.
(Klein et al., 1970).
and the three fundamental vibration frequencies of $\nu_3$ and of $\nu_4$ would be equal, and orthonormal to each other (triply degenerate bands) (Klein et al., 1970). However, the presence of other cations and anions in the lattice of apatites, promotes a distortion in the $PO_4$ tetrahedron, lowering its symmetry from $T_d$ to $C_s$ (i.e., containing now only one reflection mirror symmetry plane "m"). In the case of hydroxyapatite, the P-O distances are unequal: $P-O_1=1.538$; $P-O_2=1.537$; $P-O_3=P-O_4=1.529\,\text{Å}$ (Kay et al., 1964).

The distorted and regular tetrahedra are shown in figure 6.5. The selection rules predict for $C_s$ symmetry the following vibrations, all infrared active (Farmer, 1974 and Chakravorty and Ghosh, 1966): $\nu_1, \nu_{2a'}, \nu_{2b'}, \nu_{3a'}, \nu_{3b'}, \nu_{3c'}, \nu_{4a'}, \nu_{4b'}, \nu_{4c'}$, i.e. all nine vibrations predicted by the formula $3N-6$ appear in the infrared spectrum. The assignments of these vibrations are made by taking into consideration the fundamental vibrations of the tetrahedral "free" phosphate group. Table 6.1 is a compilation of the extensive literature available in the case of apatites, presenting only the assignments for the fundamental P-O vibrations. Besides the four fundamental modes, other bands appear in the infrared spectrum of apatites. In the case of hydroxyapatite the OH group is responsible for two additional bands. One is the fundamental vibration of the OH group occurring in the range 3560-3570 cm$^{-1}$ (Ross, 1974). The other is normally assigned to an OH libration at 630-635 cm$^{-1}$. Some difference bands are also found and the most
Table 6.1 - Vibration Spectra of Apatites: $PO_4$ Assignments.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ref.</th>
<th>$v_1$</th>
<th>$v_2$</th>
<th>$v_3$</th>
<th>$v_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA Durango</td>
<td>a</td>
<td>960</td>
<td>315,270</td>
<td>1095,1075,1040</td>
<td>603,574,566</td>
</tr>
<tr>
<td>FA natural</td>
<td>b</td>
<td>968</td>
<td>325</td>
<td>1096,1050,1025</td>
<td>605,580,565</td>
</tr>
<tr>
<td>FA Durango</td>
<td>c</td>
<td>959</td>
<td>336;305</td>
<td>1100,1071,1058</td>
<td>604,572,570</td>
</tr>
<tr>
<td>FA synthetic</td>
<td>d</td>
<td>966</td>
<td>-</td>
<td>1082,1054</td>
<td>605.5,590.5</td>
</tr>
<tr>
<td>FA RAMAN</td>
<td>d</td>
<td>-</td>
<td>-</td>
<td>1060,1034</td>
<td>617,582</td>
</tr>
<tr>
<td>FA Durango</td>
<td>e</td>
<td>962</td>
<td>472</td>
<td>1090,1038</td>
<td>601,574</td>
</tr>
<tr>
<td>FA synthetic</td>
<td>e</td>
<td>964</td>
<td>473</td>
<td>1092,1042</td>
<td>601,576</td>
</tr>
<tr>
<td>ClA synthetic</td>
<td>f</td>
<td>962</td>
<td>315</td>
<td>1092,1080,1045</td>
<td>605,570</td>
</tr>
<tr>
<td>ClA natural</td>
<td>f</td>
<td>960</td>
<td>305</td>
<td>1095,1082,1040</td>
<td>600,560</td>
</tr>
<tr>
<td>OHA synthetic</td>
<td>a</td>
<td>962</td>
<td>350,270</td>
<td>1092,1065,1028</td>
<td>603,574,564</td>
</tr>
<tr>
<td>OHA synthetic</td>
<td>g</td>
<td>962</td>
<td>255</td>
<td>1095,1055,1035</td>
<td>605,568</td>
</tr>
<tr>
<td>OHA synthetic</td>
<td>h</td>
<td>959</td>
<td>-</td>
<td>1090,1025</td>
<td>628,602,563</td>
</tr>
<tr>
<td>Cl-FA synthetic</td>
<td>i</td>
<td>962</td>
<td>340</td>
<td>1095,1090,1045</td>
<td>602,575,565</td>
</tr>
</tbody>
</table>

Notes: FA - fluorapatite; ClA - chlorapatite; OHA - hydroxyapatite; Cl-FA - fluor-chlorapatite all values are in wavenumbers (cm$^{-1}$).

Refs. a - Baddiel and Berry (1966); b - Bhatnagar (1967); c - Klein et al. (1970); d - Kravitz et al. (1968); e - Klee and Engel (1970); f - Bhatnagar (1968); g - Bhatnagar (1968a); h - Chakravorty and Ghosh (1966); i - Bhatnagar (1967a).
common is $\nu_3 - \nu_4$ occurring at 460-480cm$^{-1}$. In the case of carbonate-apatites (either mineral or biological specimens), the vibrations of the CO$_2^-$ group are also present in the spectra. According to Le Geros et al. (1970) and Montel et al. (1977) the assignments for carbonate ions in the structure of carbonate apatites are the following:

$$\nu_2 \quad 860 - 885 \text{ cm}^{-1} \quad (\text{CO}_3^{2-} \text{ in and out bending mode})$$

$$\nu_3 \quad 1465 - 1542 \text{ cm}^{-1} \quad (\text{CO}_3^{2-} \text{ stretching, carbonate apatites type A})$$

$$\nu_3 \quad 1430 - 1460 \text{ cm}^{-1} \quad (\text{same as above, carbonate apatites type B})$$

The other carbonate vibrational modes are generally absent in the infrared spectra of carbonate-apatites.

The infrared bands in the spectra of different natural apatites shown in figures 6.1 and 6.2 can now be assigned. Table 6.II presents the data from the two figures and the assignments for their respective modes of vibration.

Three of the four samples are most probably carbonate free. The Durango sample is a very well characterized example of fluorapatite and the results obtained here are in excellent agreement with previous studies (see references "a" and "e" in Table 6.I). The Ontario and Monteiro samples are also examples of fluorapatites (or fluor-chlorapatite), free of carbonate and hydroxyl, very well crystallized. The chemical analysis
presented in Table 5.1 for the Monteiro sample, definitively confirms the identification of this sample as a fluor-chlorapatite. The Ca/P molar ratio of this sample is also close to the theoretical value, viz. 1.688 (experimental) versus 1.667 (theoretical). Later in the section, X-ray diffraction, microprobe and SEM results will further characterize this mineral.

The Itataia sample clearly shows $v_3 \text{CO}_3^{2-}$ stretching vibrations. The position of these vibrations indicate that this sample is a carboante apatite of type B, i.e. the CO$_3^{2-}$ ions replace in part the PO$_4^{3-}$. The presence of carbonate in the structure of apatites can be very easily detected by I.R. spectroscopy. Even minute amounts of carbonate show the characteristic peaks, as found in this case.

Regarding the spectrum shown in figure 6.2, most bands can be assigned to phosphate, carbonate and hydroxyl groups occurring in hydroxyapatite (see Table 6.II). The very characteristic hydroxyapatite band (OH stretching) is definitely present at 3566 cm$^{-1}$. This band can be regarded as an indication of the crystallization of the sample. It is absent in amorphous apatites. The other I.R. signals appearing in figure 6.2 can receive different assignments. The water peaks for instance, occurring at approximately 3400 cm$^{-1}$ (broad) and in the range from 1620 to 1680cm$^{-1}$ can result from the absorption of atmospheric water vapour during the preparation of the KBr pellet.
TABLE 6.II - Assignments of the I.R. vibration modes of apatites (spectra shown in figures 6.1 and 6.2).

VIBRATIONS (cm$^{-1}$)

<table>
<thead>
<tr>
<th>SAMPLES</th>
<th>$\nu_1$</th>
<th>$(\nu_3^- \nu_4^-)$*</th>
<th>$\nu_3$</th>
<th>$\nu_4$</th>
<th>$\nu_2$</th>
<th>$\nu_3$</th>
<th>$\nu_5$</th>
<th>$\nu_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Durango</td>
<td>963</td>
<td>462</td>
<td>1095,1045</td>
<td>606,577,551</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Itataia</td>
<td>963</td>
<td>456</td>
<td>1095,1044</td>
<td>606,577,550</td>
<td>-</td>
<td>1460,1422</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Monteiro</td>
<td>963</td>
<td>456</td>
<td>1093,1042</td>
<td>605,577,551</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ontario</td>
<td>959</td>
<td>460</td>
<td>1097,1047</td>
<td>608,574,546</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hydroxyapatite</td>
<td>-</td>
<td>460</td>
<td>1101,1039</td>
<td>608,576,540</td>
<td>827</td>
<td>1451,1416</td>
<td>3566(**)</td>
<td></td>
</tr>
</tbody>
</table>

(*) although there is some discussion in the literature concerning this vibration, the assignment of a difference band is the most accepted at this stage (Casciani and Condrate, 1980).

(**) there is a shoulder in the region where the libration mode is expected.
can also be a consequence of the high surface area of this sample and its hygroscopic behaviour. The peaks occurring at 787 cm\(^{-1}\) and 750 cm\(^{-1}\) can not be assigned to hydroxyapatite, however. It is possible that the sample is contaminated by other phosphate phases. Monetite (CaH\(_2\)PO\(_4\)) and brushite (CaH\(_2\)PO\(_4\).2H\(_2\)O) present OH out-of-plane bending vibrations respectively in the ranges of 700-790 cm\(^{-1}\) and 750-785 cm\(^{-1}\) (Ross, 1974; Casciani and Condrate, 1980). Another possibility is the interlayering of octacalcium phosphate with hydroxyapatite found in some synthetic samples. This would explain the broad water peak and the water bands previously mentioned, all of them occurring in the spectrum of octacalcium phosphate. Also present in this compound are some in-plane bending of P-O-P in the range 1200-1295 cm\(^{-1}\). These bands are present in the spectrum in the figure 6.2 (not marked) (LeGeros, R. and LeGeros, J., 1984). Since this sample was used only in a few experiments in this thesis, no further studies on the characterization were pursued.

In the spectra of quartz and kaolinite (figures 6.3 and 6.4), the assignment of the peaks to their respective vibration modes is summarized in Table 6.III. Both spectra show the characteristic peaks accepted for the two minerals in question and are in good agreement with published data (see for example Farmer, 1974; Moenke, 1974; de Araujo, 1982).
<table>
<thead>
<tr>
<th>Vibrations (cm(^{-1}))</th>
<th>Quartz (α form)</th>
<th>Kaolinite</th>
</tr>
</thead>
<tbody>
<tr>
<td>3691,3665,3648,3615</td>
<td>not present</td>
<td>OH stretching</td>
</tr>
<tr>
<td>1171,1143,1087</td>
<td>Si-O-Si antisymmetric stretching</td>
<td>Si-O-Si symmetric stretching</td>
</tr>
<tr>
<td>1114</td>
<td>Si-O perpendicular stretching</td>
<td></td>
</tr>
<tr>
<td>1099,1034,1007</td>
<td>Si-O-Si antisymmetric stretching</td>
<td>Si-O-Si symmetric stretching</td>
</tr>
<tr>
<td>936</td>
<td>not present</td>
<td>surface OH bending</td>
</tr>
<tr>
<td>912</td>
<td>not present</td>
<td>inner OH bending</td>
</tr>
<tr>
<td>799,779</td>
<td>Si-O-Si symmetric stretching</td>
<td>Si-O-Si symmetric stretching</td>
</tr>
<tr>
<td>790</td>
<td>Si-O-Si symmetric stretching</td>
<td></td>
</tr>
<tr>
<td>753,692</td>
<td>not present</td>
<td>surface OH libration</td>
</tr>
<tr>
<td>692</td>
<td>&quot;T-O-T&quot; symmetric stretching</td>
<td>not present</td>
</tr>
<tr>
<td>516,453,415</td>
<td>O-Si-O bending</td>
<td>O-Si-O bending</td>
</tr>
<tr>
<td>495,447</td>
<td>O-Si-O bending</td>
<td></td>
</tr>
<tr>
<td>385,362</td>
<td>lattice vibrations</td>
<td>lattice vibrations</td>
</tr>
<tr>
<td>334</td>
<td>lattice vibrations</td>
<td></td>
</tr>
</tbody>
</table>

Note: the kaolinite band at 602 cm\(^{-1}\) cannot be assigned to any fundamental vibration mode. It is probably a combination band.
Other Techniques

Some mineral samples were submitted, in a preliminary phase, to characterization by X-ray diffraction, electron microprobe (JEOL, model JXA-3A) and scanning electron microscope (ETEC-Autoscan equipped with an EDX X-ray spectrometer). The results described below refer to only the Monteiro apatite sample. Details on the work performed on the other mineral samples are given in appendix I.

a) - X-ray diffraction

The X-ray diffractogram of the sample exhibits all the main "d" lines for fluorapatite. The three strongest lines are situated at 2.83, 2.73 and 2.79Å. These values are relatively close to the tabulated lines for fluorapatite, viz, 2.80, 2.702, 2.772Å (see Nriagu, 1984 and Table 4.II). No lines from any other mineral phase were present in the diffractogram obtained.

b) - Electron Microprobe

Elemental mapping of polished Monteiro apatite grains showed the presence of Ca and P. The elements were evenly distributed over the mineral grains tested. No contaminant elements were found in the grains examined.

c) - EDX/SEM

In addition to the electron microprobe elemental mapping, some Monteiro apatite grains were also examined in a ETEC Autoscan scanning electron microscope, equipped with an energy-dispersive X-ray spectrometer. The use of energy-
dispersive spectrometers has some advantages in comparison to wavelength-dispersive spectrometers (WDS) as the one in the JEOL microprobe. Among other advantages, energy-dispersive spectrometers have a higher sensitivity. In fact, the energy-dispersive spectrum of the Monteiro apatite sample showed the presence of chlorine in addition to Ca and P (fluorine could not be detected because of its low atomic number). No other elements were found.

In conclusion, the use of other characterization techniques confirmed the infrared and chemical analyses identification of the Monteiro apatite sample as being an almost pure example of fluor-chlorapatite. Throughout this thesis the sample will be referred to as fluorapatite only, due to its much larger fluorine content in comparison to chlorine.

6.1.2 - Sizing and Surface Area Measurement

Quartz and Fluorapatite (Monteiro) -38μm samples have their size distributions (as cumulative % above size) shown in figures 6.6 and 6.7. The log mean size of the two size distributions, automatically calculated by the Elzone apparatus, were 14.41μm for fluorapatite and 13.45μm for quartz. The Elzone assumes a log normal size distribution for size data. Below and above size d95 values were found to be the following, respectively: 34μm and 5μm for quartz and 38μm and 3μm for fluorapatite. The size distributions
Figure 6.6 - Size Distribution of Fluorapatite.
Figure 6.7 - Size Distribution of Quartz.
obtained for two the minerals are very similar in the size range analysed by the Elzone.

Part of the -38μm fluorapatite sample was split at a nominal cut size of 6μm by standard beaker decantation technique (assuming spherical particles with Stokesian behaviour). The above size cumulative size distribution of the non-settling material is shown in figure 6.8. The calculated log mean size was 4.88μm and the d95 below and above size values were respectively 16μm and 1μm. This sample was only used in the sedimentation tube test programme. The preparation of this finer fluorapatite sample was conducted to make the size range compatible for comparison with the kaolinite sample used in the same test programme. The kaolinite sample was not subjected to any sizing preparation or analysis. The manufacturer's size specifications are the following: 55-65% by wt. below 2μm, mean size of 1.1μm, and 0.20% maximum of +100μm.

Surface area determinations were made by applying the standard multipoint BET technique. Pure nitrogen was used as adsorbent and pure argon as carrier. Adsorption of nitrogen was accomplished at liquid nitrogen temperature. The results are summarized in Table 6.IV. They indicate that although the Elzone size distribution results for quartz and fluorapatite are similar in the size range analysed, the specific surface area of the quartz sample is approximately 51% of that of the fluorapatite sample. The specific surface area values shown in Table 6.IV were utilized in the
Figure 6.8 - Size Distribution of Fluorapatite (beaker decantation "overflow").
## TABLE 6.IV - BET Surface Area Determinations

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Sample wt. (g)</th>
<th>no. of points</th>
<th>CC*</th>
<th>total area $m^2$</th>
<th>specific surface area $m^2/g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorapatite</td>
<td>0.3168</td>
<td>4</td>
<td>0.946</td>
<td>0.329</td>
<td>1.037</td>
</tr>
<tr>
<td>Quartz</td>
<td>0.8990</td>
<td>4</td>
<td>0.981</td>
<td>0.478</td>
<td>0.531</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>0.3910</td>
<td>4</td>
<td>0.995</td>
<td>6.692</td>
<td>17.115</td>
</tr>
</tbody>
</table>

(*) CC = linear regression correlation coefficient
testwork described later (see section 6.4).

6.1.3 - Electrophoresis and Related Work

Knowledge of the interfacial electrical properties of minerals is very relevant in most applied surface chemistry work. In this section, microelectrophoretic tests and related experiments are presented.

Figure 6.9 shows the electrophoretic mobility(*) of fluorapatite (Monteiro) as a function of pH in distilled water and in KCl solution (indifferent electrolyte). In both solutions an iep (pH) occurs at approximately pH 4.1. Such a value is relatively common for natural apatites. This iep(pH) should be considered as a "non-equilibrium" iep since the total length of time involved in the test runs was less than 4 hours. Dilute KOH and HCl solutions were used for pH regulation.

Both curves in figure 6.9 show an increase in the absolute negative value of the electrophoretic mobility (E.M.) as the pH is increased above the iep(pH). This is more accentuated in pH range from 4 to 9. Above pH 9, the absolute value of the E.M. continues to increase but at a much smaller pace. The maximum E.M. absolute value assumed by the

(*) - It is usual to see microelectrophoretic results for mineral system presented as zeta potential values, generally calculated assuming valid the Helmholtz-Smoluchowski equation (Anon., 1975). This practice will be avoided in the present thesis because of possible theoretical objections related to the applicability of the H.S. treatment.
Figure 6.9 - Electrophoretic Mobility of Fluorapatite as a Function of pH.
samples is approximately 2.7\(\mu\)m/s per volt/cm\(^{*}\) in distilled water at pH 10.4 to 11.

Figure 6.10 depicts the E.M./pH relationship for the synthetic hydroxyapatite sample in distilled water. As in figure 6.9 one can clearly find an iep(pH) located now at approximately pH7, in very good agreement with the data presented in table 4.V. The E.M. values for hydroxyapatite are always smaller in absolute value than those encountered for fluorapatite. The shape of two E.M./pH curves are comparable, however.

Many different ubiquitous ions occur in mineral aqueous systems. The important contributions of these ions should not be disregarded whenever aqueous mineral processing separations are involved. Although the presence of such ionic species is generally unavoidable, there are some remedies. For instance, the sometimes unexplained need for different "dispersants" and "depressants" in flotation systems, is most probably related to the presence of such ionic species. Many of the reagents introduced also act as complexing or sequestering agents, controlling the concentration of the ubiquitous ions.

Figure 6.11 depicts the dramatic effect of Al aqueous species on the E.M. of fluorapatite as a function of pH. Even minute amounts (5 \(\times\) 10\(^{-6}\) mol/litre or approx.\(^{(*)}\) - the unit of the E.M. should convey the idea of rate of travel of the particles (length/time) based on a standard gradient in electrical field through the electrophoresis cell of one volt per unit of length.
Figure 6.10 - Electrophoretic Mobility of Hydroxyapatite as a Function of pH.
Figure 6.11 - Effect of Al Aqueous Species on the Electrophoretic Mobility of Fluorapatite.
1.2ppm) of these aqueous species are able to change the E.M. curve of fluorapatite completely. A more detailed discussion of the mechanisms involved in such changes is outside the scope of this work (see for example James and Healy, 1972 and Senior, 1987). In the specific case of Al species, there is strong experimental evidence for the presence of highly solvated species at the interface. The pH range for maximum E.M. is the same range reported by de Araujo (1982) for maximum adsorption of Al species onto a quartz surface. As the surface becomes negative (charge reversal 3 in the James and Healy model), at the highest AlCl$_3$ concentration, the reversal occurs at a higher pH value (pH=8.2) than for the lowest AlCl$_3$ concentration (at 6.5). This is in agreement with the James and Healy model.

In both cases, under alkaline conditions, the curves in the presence of Al species approximate the base curve (which is the KCl curve, since the tests involving AlCl$_3$ were also performed in the presence of $1 \times 10^{-4}$ mol/litre KCl).

Figure 6.12 shows the effect of Mg and Ca ionic species on the E.M./pH relationship of fluorapatite. Only one concentration level was tested ($1 \times 10^{-3}$ mol/litre MgCl$_2$ and CaCl$_2$). The behaviour of these two bivalent ions is different from that of Al (trivalent). The ionic species distribution pH diagrams calculated by Senior (1987) show the pH for hydroxide precipitation and the mole % of the different aqueous Al, Mg and Ca species, at different salt
Figure 6.12 - Effect of Ca and Mg Ionic Species on the Electrophoretic Mobility of Fluorapatite.
concentrations. This type of diagram has been used to correlate the changes in E.M. values with changes in the metallic ionic species present in solutions. The pH value where the first hydroxo-complex starts forming in solution is similar to the pH value where there is the first charge reversal above the substrate's iep(pH) (namely CR2 in the James and Healy model). This correlation holds relatively well in the case of Ca and Mg on fluorapatite but it does not apply to the Al case. One alternative line of thinking was introduced by Somasundaran (1984). It objects to the correlation between the diagrams calculated for bulk ionic species and the observed changes in the electrophoretic mobilities of minerals in contact with such ions. According to Somasudaran (1984), at the mineral solution interface, the activities of the ionic species are different. This situation would explain some discrepancies between expected and experimental results. One can speculate on the possibility for the precipitation of the metal hydroxide to occur at lower pH and concentration level at the interface. This is also expected if the nucleation role of the substrate is taken into consideration.

The Mg-fluorapatite curve shown in figure 6.12 presents an extra peculiarity. In general, the available literature does not show data points above the pH of maximum positive E.M. In figure 6.12 one can see that the micro-electrophoretic mobility decreases above pH 11 but the curve does not return to its original shape. This aspect addresses
another still not completely answered question: after adsorption and metal hydroxide precipitation (or "condensation"), does the adsorbed species desorb as the pH is increased? According to the results already mentioned of de Araujo (1982), for the Al-quartz system there is desorption as the pH increases. Similar behaviour was reported by Cooke (1953) for the Ca-quartz system. The return to the original E.M./pH base curve for the Al-fluorapatite system shown in figure 6.11, seems to suggest that desorption actually takes place. At higher pH conditions, such as in the Mg-fluorapatite system, the ionic strength of the medium may hinder the desorption.

The Ca-fluorapatite curve presents another complicating factor: Ca is a pdi for this system. Literature results in the presence of $1 \times 10^{-2}$ mol/dm$^3$ of Ca(NO$_3$)$_2$ on fluorapatite show zeta potential values always positive in all pH ranges tested (Somasundaran and Agar, 1972). In figure 6.1 up to pH 13 the E.M. of fluorapatite in the presence of a concentration of Ca ionic species 10 times smaller than that of Somasundasan and Agar shows only negative values. Although one can argue that the concentration difference is solely responsible for the observed behaviour, the techniques utilized in each case are different. The cited results were obtained by streaming potential using a plug of coarse (greater than 200μm) fluorapatite particles. In the case of microelectrophoresis, a suspension of very fine particles is employed. The surface areas available for adsorption can be
quite different. It is probably higher in the case of microelectrophoresis. Of course the concentration effect plays, likely, a dominant role but the differences in the techniques should also be accounted for when comparing results. At such a high pH, compression of the double layer should also be considered.

Figure 6.13 shows E.M. results for quartz in the presence of Al, Mg, and Ca aqueous species as a function of pH. These results are included for comparison purposes. In the same figure, the E.M./pH curves for quartz in distilled water and KCl (1x10^{-4}mol/dm^3) are also depicted. This quartz sample shows absolute negative E.M. values greater than those found for fluorapatite both in distilled water and in KCl solution. The Al-quartz system presents a behaviour similar to that of fluorapatite, but for the lowest metal salt concentration there is no change in the sign of the E.M. This can be explained by the higher E.M. absolute negative value for quartz. The Mg and Ca systems also show a similar behaviour to that of fluorapatite, especially in the case of Mg. Although there is a difference in Mg concentration (twice larger in the quartz case), the position of CR2 (from James and Healy model) is only 0.2 pH units smaller and the shape of the curves up to pH 11 is almost identical.

For completeness, Figure 6.14 shows the E.M./pH curve for kaolinite in distilled water. Over the entire pH range tested, the sample shows negative E.M. with a minimum
Figure 6.13 - Effect of Al, Ca and Mg Species on the Electrophoretic Mobility of Quartz.
Figure 6.14 - Electrophoretic Mobility of Kaolinite as a Function of pH.
(in absolute value) occurring at approximately pH 3.5. Clay minerals such as kaolinite develop electrical surface charge by two distinct mechanisms (Parks, 1975). The charge on the basal planes of kaolinite is structural and always negative, independently of the pH. At the crystal edges however, the charge is pH dependent. The overall charge result is the combination of these two charges. More details on the surface charge generation on clays can be found elsewhere (Parks, 1975; van Olphen, 1971).

The pzc of the Monteiro fluorapatite sample was determined by two different procedures: Mular and Roberts (1966) and Ahmed (1966). Figure 6.15 depicts the results obtained by applying the Mular and Roberts procedure. The ΔpH/final pH curves were obtained under distinct conditions (see figure for details). They have a common intersection point at ca. pH 7. This value for the pzc(pH) of fluorapatite is in good agreement with the results presented in table 4.V. The Ahmed time/pH drift technique confirms the value obtained by the Mular and Roberts procedure. Ahmed's procedure results are presented in table 6.V.

6.1.4 - Dispersion Studies

Qualitative studies on the dispersion of fluorapatite (Monteiro), quartz and kaolinite suspensions were conducted. These tests were performed for two main
Figure 6.15 - Determination of the pzc(pH) of Fluorapatite by the Mular and Roberts Method.
TABLE 6.V - Determination of the pzc(pH) of Fluorapatite by the Ahmed's Method

Conditions: sample particle size -38μm; 1 x 10^{-2}mol/l KCl;
for long equilibration times samples were kept under N₂.

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<th>3</th>
<th>4</th>
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<td>7.7</td>
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<td>-</td>
<td>7.9</td>
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<td>9.7</td>
<td>9.6</td>
<td>9.5</td>
<td>-</td>
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<td>9.2</td>
<td>8.6</td>
<td>7.6</td>
<td>7.2</td>
<td>7.2</td>
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<td>7.1</td>
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<td>7.1</td>
</tr>
</tbody>
</table>
reasons:

(i) - to limit the pH range for adsorption, flocculation and flotation studies;

(ii) - to investigate the stability of mineral suspensions, an important aspect in almost all physico-chemical mineral processing operations.

In all tests reported in this section, the % transmittance to light at 450nm (Spectronic 21), measured after a pre-established settling period of the mineral suspension under investigation, was employed as an indication of the degree of dispersion/aggregation of the suspension. The mineral samples used were the same samples used for most of the work reported in this thesis, namely quartz -38μm, fluorapatite (Monteiro) -38μm and kaolinite, mean size =1.1μm. Since the size ranges of the these three mineral samples were different, and the settling periods were selected arbitrarily to give measurable % transmittance values, the tests are comparable only for each mineral. The % transmittance in the case of kaolinite, for instance, was measured after longer settling periods than for other minerals. It should be pointed out that differences in reflectivity and shapes of the mineral particles involved in this type of measurement can alter the results immensely. The tests have therefore a qualitative character, indicating the pH range for maximum/minimum stability and effect of dispersants in terms of improving or worsening the degree of
dispersion as compared to tests made in their absence.

Figure 6.16 shows the effect of pH on the stability of a fluorapatite suspension. In the alkaline region, the effect of three different pH modifiers is shown (HCl dilute solution was used to reach acid pH values). This figure clearly shows an increase in the degree of dispersion of the suspension as the pH is increased (smaller % transmittance values). KOH and NaOH had the same effect on the stability of this mineral. Ammonium hydroxide (NH$_4$OH) however, showed a more pronounced effect, notably at pH 11. Ammonium hydroxide is known to provide stronger dispersion in certain iron ore pulps (Bretas, 1980, private communication). At the moment, the mechanisms behind this phenomenon are not known.

Figure 6.17 shows the results obtained with quartz. The stability also increased as the pH increases. The magnitude of the increase was smaller than in the case of fluorapatite. The same effect of NH$_4$ was also observed in this case. If figures 6.16 and 6.17 are compared to the E.M./pH curves already shown (figure 6.97 for fluorapatite and 6.13 for quartz), it is evident that they present the same general trend, i.e. the larger the absolute negative E.M. value the smaller is the % transmittance value (greater dispersion). The smaller magnitude of the variation in case % transmittance/pH curve for quartz may be related to the fact that quartz possesses higher absolute negative values of its electrokinetic (zeta) potential than fluorapatite for a given pH range. One should recall that absolute values of
Figure 6.16 - Stability of Fluorapatite Suspensions as a Function of pH.
Figure 6.17 - Stability of Quartz Suspensions as a Function of pH.
% transmittance can not be compared between two minerals. The two curves for two different settling periods shown in figure 6.18 demonstrate the importance of this parameter.

Figure 6.18 presents the % transmittance/pH curve for kaolinite. Again two different settling periods are displayed. The E.M./pH curve for this mineral, shown in figure 6.14 was replotted in figure 6.18. This diagram exhibits a direct correlation between electrophoretic mobilities (or zeta potentials) and % transmittance in this case. High stability of a mineral suspension is associated with high negative values of zeta potential (repulsion term of the total interaction energy calculated by the DLVO theory). The measurement of % transmittance is a useful technique when a rough estimate of the stability of a suspension is required. As seen, it can provide the same information as obtained by a more sophisticated technique such as electrophoresis.

Table 6 VI shows a compilation of tests made with the three minerals in the presence of many commonly used dispersants. The pH range selected for these tests is limited to the alkaline range, from pH 9 to pH 11. This pH range is the one where maximum dispersion was observed for all minerals tested. The values in table 6.VI should be compared for each mineral with the base value obtained with KOH as pH modifier. Among the dispersants selected for testing (Na sesquisilicate - METSO 99, Na pyrophosphate, Na tripolyphosphate, Na hexametaphosphate, Na borate - BORAX and
Figure 6.18 - Stability of Kaolinite Suspensions as a Function of pH.
Table 6.VI - Action of Selected Dispersants on the Stability of Mineral Suspensions

<table>
<thead>
<tr>
<th>Mineral (settling time)</th>
<th>pH base value</th>
<th>NH&lt;sub&gt;4&lt;/sub&gt;OH</th>
<th>METSO 99 (KOH)</th>
<th>SPP (KOH)</th>
<th>STPP (KOH)</th>
<th>STPP (NH&lt;sub&gt;4&lt;/sub&gt;OH)</th>
<th>SHMP (KOH)</th>
<th>SHMP (NH&lt;sub&gt;4&lt;/sub&gt;OH)</th>
<th>STB (KOH)</th>
<th>STB (NH&lt;sub&gt;4&lt;/sub&gt;OH)</th>
<th>EDTA (KOH)</th>
<th>EDTA (NH&lt;sub&gt;4&lt;/sub&gt;OH)</th>
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</thead>
<tbody>
<tr>
<td>Fluorapatite (2 hrs.)</td>
<td>9</td>
<td>49</td>
<td>43</td>
<td>34</td>
<td>12</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kaolinite (2 hrs.)</td>
<td>9</td>
<td>4</td>
<td>-</td>
<td>2</td>
<td>1</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>4</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>4</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>0.5</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>2</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kaolinite (24 hrs.)</td>
<td>11</td>
<td>20</td>
<td>13</td>
<td>11</td>
<td>11</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>13</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

(*) Concentration of dispersants is 100 mg/l except for NH<sub>4</sub>OH (measured by the pH value).

abbreviations: METSO 99 = hydrated Na sesquisilicate  SPP = Na pyrophosphate
STPP = Na trypolyphosphate  SHMP = Na hexametaphosphate
STB = Na tetraborate (borax)  EDTA = salt of ethylenediaminetetraacetic acid
EDTA). Sodium silicates and phosphates are among the most commonly used dispersants for mineral pulps. The two other dispersants are not conventionally used for these purposes. Borax has some cost advantages compared to the phosphate based dispersants. It may also be less dangerous in terms of its effects on fresh water lakes. The organic complexing agent tested—EDTA, was used to make comparisons. A second reason for testing EDTA was to shed some light on the mechanisms involved in the dispersing action of these reagents.

From the results presented in table 6.VI the following points should be emphasized:

(i) - at the concentration level tested all dispersants increased the degree of dispersion of fluorapatite and kaolinite, regardless of pH. For quartz there were three exceptions to this general rule, EDTA, STPP and STB, all with KOH as the pH modifier.

(ii) - In tests in which KOH regulated the pH, the following order of increasing dispersing power was found for each mineral at pH 9:
- fluorapatite EDTA<METSO 99<STPP<SHMP<SPP.
- quartz EDTA<STPP<METSO 99<SHMP<SPP.
- kaolinite METSO 99<SPP= STPP= SHMP= EDTA

At pH 11:
- fluorapatite METSO 99<STPP<EDTA SPP<SHMP.
-quartz STB< STPP< EDTA< METSO 99< SHMP.
-kaolinite STB< METSO 99= SPP= STPP= EDTA< SHMP.

(iii) - as in (ii) but in NH₄OH pH regulated tests at pH 9:
-fluorapatite EDTA= STPP< SHMP.
-quartz STPP< EDTA< SHMP.

At pH 11:
-fluorapatite EDTA< SPP= STPP< STB= SHMP.
-quartz EDTA< SPP = SHMP< STB.
-kaolinite STB< EDTA< SPP =SHMP.

(iv) - all tests using ammonium hydroxide for pH regulation showed improved dispersion as compared to KOH, for the three minerals in all pH conditions tested. In some cases, NH₄OH was a stronger dispersant than Na silicate, EDTA or Na tripolyphosphate.

To help in the understanding of the dispersing mechanisms, some microelectrophoretic tests were performed in the presence of some selected dispersants, for both quartz and fluorapatite. They are summarized in table 6.VII. In all cases, the absolute values of electrophoretic mobilities were increased. The increase in E.M. for both minerals are in almost complete agreement with the results shown in table
TABLE 6.VII - Electrophoretic Mobilities of Quartz and Flourapatite in the Presence of Selected Dispersants

<table>
<thead>
<tr>
<th>Mineral</th>
<th>KOH base value (pH)</th>
<th>NH₄ (lg/1)</th>
<th>METSO 99 (lg/1)</th>
<th>STB/KOH (lg/1)</th>
<th>SHMP/KOH (lg/1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 10</td>
<td>-4</td>
<td>-5.4</td>
<td>-4.8</td>
<td>-</td>
<td>-4.7</td>
</tr>
<tr>
<td>pH 11</td>
<td>-3.8</td>
<td>-7.1</td>
<td>-6.3</td>
<td>-4.8</td>
<td>-6.8</td>
</tr>
<tr>
<td>Flourapatite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 10</td>
<td>-2.6</td>
<td>-2.9</td>
<td>-2.7</td>
<td>-2.8</td>
<td>-3.2</td>
</tr>
<tr>
<td>pH 11</td>
<td>-2.7</td>
<td>-3.3</td>
<td>-3.4</td>
<td>-3.25</td>
<td>-3.6</td>
</tr>
</tbody>
</table>

(*) See TABLE 6.VI for abbreviations.
6. VII. Sodium silicates are dispersants that act through a protective colloid action, covering the particle completely and creating a new electrical double layer (Klassen and Mokrousov, 1963).

In the case of polyphosphates (and probably also for borates), dispersant ions adsorb specifically (chemical forces) onto certain minerals, such as hematite (Breeuswma and Lyklema, 1973). Similar reports can be found in the literature for other minerals. For apatite, Parsonage et al. (1984) observed a large increase in the negative values of the zeta potential of this mineral in the presence of Na silicate and Na tripolyphosphate (the largest increase was in the latter case which agrees with the results reported herein). Parsonage et al. (1984) agrees on the adsorption of Na silicate promoting dispersion through a protective colloid mechanism, but they refrain from extending this mechanism to the action of tripolyphosphate.

Without any further experimental work (which would be outside the scope of this thesis) the only conclusions that can be drawn at this stage are:

(i) - alkaline pH values, which result from additions of NaOH, KOH or NH₄OH, increase the stability of the suspensions of the three minerals tested. This increased stability seems to be related directly to an increase in the negative value of zeta
potential of the particles. The anomalous behaviour of NH₄OH defies explanation without further testing;

(ii) - in systems where KOH was used as the pH modifier, Na hexametaphosphate shows the strongest dispersion power at pH 11 and Na pyrophosphate at pH 9 (generally closely followed by SHMP):

(iii) - for tests in which NH₄ was used, SHMP is the strongest dispersant at the pH levels tested, except for quartz at pH 11, where it is second after Na tetraborate.

(iv) - as a general rule, dispersants cause an increase in E.M. abs. values. The work performed can not, however, ascertain the mechanisms through which the dispersants act. Protective colloidal and chelation actions are two of the possibilities. The anomalous behaviour of NH₄OH deserve further experimental work.

As a summary of this mineral characterization section the following points are presented:

(i) - infrared spectroscopy (Section 6.1.1) was
successfully used as the main mineral characterization technique. It proved to be very applicable, especially for apatites. Infrared spectroscopy of minerals is a very powerful identification and characterization technique. It is not widely used in the mineralogical field because it has to compete with more traditional methods such as X-ray diffraction. Nevertheless, it can give information accurately and as quickly as any other more conventional techniques;

(ii) - microelectrophoresis (section 6.1.2), sizing and surface area measurements (section 6.1.3) and dispersion studies (section 6.1.4) provided important information on the interfacial behaviour of the minerals tested. This information will be frequently referred to in the next sections;

(iii) - although some points will be left unanswered (e.g. dispersant/mineral mechanisms), they are outside of the scope of the work reported here. Nevertheless, experimental facts are useful in terms of the overall knowledge concerning the systems under study.
6.2 - Characterization of Starches

The characterization studies on starches reported herein should be viewed as complimentary information to that provided in the review section 4.4. It is not an exhaustive characterization programme. Only important aspects, considered relevant for this thesis, were the object of study.

6.2.1 - Infrared Spectroscopy(*)

Infrared spectroscopic techniques are widely employed in organic chemistry. Extensive literature is available, covering both theoretical and practical aspects of infrared spectroscopy as applied to the identification and characterization of organic compounds (e.g. Bellamy, 1958 and 1968; Nakanishi, 1962; Rao, 1963; Silverstein and co-workers, 1979).

In the case of starches and related compounds, the available infrared literature is more restricted, although for carbohydrates in general there is considerable amount of published work (Mathlouthi and Koenig, 1986). In the present work, the building block of starches, viz. α-D-Glucose, was characterized first. All infrared vibrations present in α-D-Glucose molecules are expected to be also present in the

(*) - Infrared spectra of the two surfactants used in the present work were also recorded. They are discussed separately in Appendix II.
infrared spectra of starches. While it is not expected that these bands remain unaffected in the spectra of the polymers, knowledge of the spectral features of the oxygenated ring system of α-D-Glucose would be of great help (Rao, 1962). A survey of published data on the spectra of α-D-Glucose is given in Table 6.VIII. An analysis of this table shows the complexity of the infrared spectrum of this compound. Although α-D-Glucose is formed by three types of atoms only, the structure of the molecule is such that many infrared active bands are present in the spectrum. The heteroatomic ring structure itself is responsible for some important infrared bands. According to Rao (1963), the absorption bands occurring at approximately 915 cm\(^{-1}\) and 770 cm\(^{-1}\) (ring stretching vibration and symmetrical ring breathing vibration, respectively) will vary according to the type of linkages present in polymers built from α-D-Glucose units. For example, for α-D-Glucose linkages, there is a gradual increase from 907 cm\(^{-1}\) to 930 cm\(^{-1}\) for type I vibration (ring stretching) and a decrease for type III (ring breathing) from 770 cm\(^{-1}\) to 760 cm\(^{-1}\). According to Zhbankov (1966), type II vibration (C-H deformation at 840-850 cm\(^{-1}\)) can be used, in some cases, as indicative of the α-D anomeric form of glucose (i.e. C\(_5\) hydrogen occupies an equatorial position in the chair configuration rather than an axial position). In the case of the β-D anomer, type II vibration shows a peak at a higher frequency, approximately at 890 cm\(^{-1}\). Type III vibration is also shifted in β-D-Glucose to a lower frequency.
### TABLE 6.VIII - Infrared Absorption Bands of α-D-Glucose (*)

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Intensity(**)</th>
<th>Assignment(**)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3300-3420</td>
<td>s(broad)</td>
<td>OH str. (intra/intermolecular H bonding)</td>
</tr>
<tr>
<td>2950</td>
<td>s(sharp)</td>
<td>CH asym.str.CH(_2)</td>
</tr>
<tr>
<td>2850</td>
<td>s(sharp)</td>
<td>CH sym.str.CH(_2)</td>
</tr>
<tr>
<td>1640</td>
<td>w to m</td>
<td>H(_2)O adsorbed (H-O-H flexion)</td>
</tr>
<tr>
<td>1460</td>
<td>s</td>
<td>OH i.p. bending or CH(_2) internal def (scissoring?)</td>
</tr>
<tr>
<td>1370</td>
<td>s</td>
<td>CH bending</td>
</tr>
<tr>
<td>1330</td>
<td>m</td>
<td>OH i.p. bending mixed with CH str.</td>
</tr>
<tr>
<td>1280</td>
<td>m to w</td>
<td>CH bending</td>
</tr>
<tr>
<td>1215</td>
<td>m</td>
<td>OH i.p. bending or CH(_2) def (wagging?)</td>
</tr>
<tr>
<td>1195</td>
<td>m</td>
<td>OH i.p. bending</td>
</tr>
<tr>
<td>1140</td>
<td>s</td>
<td>asym.str. C-O-C bridge</td>
</tr>
<tr>
<td>1105</td>
<td>s</td>
<td>asym. in phase ring str.</td>
</tr>
<tr>
<td>1070</td>
<td>w</td>
<td>COH str.</td>
</tr>
<tr>
<td>1050,1015</td>
<td>m to s</td>
<td>CO str.</td>
</tr>
<tr>
<td>990</td>
<td>m</td>
<td>CO str.</td>
</tr>
<tr>
<td>915</td>
<td>m</td>
<td>ring str. vibration</td>
</tr>
<tr>
<td>840-850</td>
<td>m</td>
<td>CH def in anomeric form</td>
</tr>
<tr>
<td>760-770</td>
<td>m</td>
<td>sym. ring breathing vibration</td>
</tr>
<tr>
<td>740</td>
<td>w</td>
<td>CH(_2) rocking def (?)</td>
</tr>
<tr>
<td>400-700 (many)</td>
<td>w to m</td>
<td>mainly OH o.o.p. bending</td>
</tr>
</tbody>
</table>


(**) abbreviations: s = strong; m = medium; w = weak asym. = asymmetric; sym = symmetric; str. = stretching; def = deformation i.p. = in plane; o.o.p. = out of plane
of approximately $715\text{cm}^{-1}$. In addition to these three bands, the position of the OH stretching bands can also be used as indicative of the anomeric form of glucose (Zhbankov, 1966). The $\alpha$-D anomer has the C$_5$ hydroxyl in the axial position. This gives rise to intermolecular OH stretching frequencies at approximately $3410\text{cm}^{-1}$ and $3320\text{cm}^{-1}$. Since this region of the spectrum is generally treated as one strong and broad peak, the fine structure of the peak is sometimes overlooked.

Figure 6.19 shows the infrared spectrum of $\alpha$-D(+) Glucose (BDH Chemicals) obtained by the KBr pellet method. All main adsorption peaks discussed in table 6.VIII are present in the spectrum shown in fig. 6.19. The broad OH stretching band from $3450\text{cm}^{-1}$ to $3200 \text{cm}^{-1}$, centered approximately at $3300\text{cm}^{-1}$ is comprised of many individual peaks. Two of them are situated at $3406\text{cm}^{-1}$ and $3318\text{cm}^{-1}$, in close agreement with the results presented by Zhbankov (1966), indicating the $\alpha$-D anomeric form. This is also confirmed by the position of the type II vibration (Rao, 1963 and Zhbankov, 1966) at $837\text{cm}^{-1}$. In addition to the bands already discussed in table 6.VIII, a few other bands appear in the spectrum shown in fig 6.19. The absorption at $2354\text{cm}^{-1}$ is a spurious band due to atmospheric CO$_2$ (caused by an unbalanced spectrophotometer). Two other bands occurring at $1559\text{cm}^{-1}$ and $1521\text{cm}^{-1}$ can be associated with a protein type impurity in the sample (see the discussion on starch spectra). Small peaks (not marked in figure 6.19) in the
Figure 6.19 - Infrared Spectrum of $\alpha$D(+)-Glucose.
1700-1800 cm\(^{-1}\) wavenumber range can be associated with carboxylic acid impurities.

Figures 6.20 to 6.23 show the infrared spectra (KBr pellets, best results) of the many starch samples used in the present work. One common characteristic of all starch spectra is the much smaller definition of most of the peaks as compared to the spectrum of \(\alpha\)-D(+) Glucose.

To simplify the interpretation of starch spectra the various groups responsible for the infrared bands are discussed separately:

(i) \(-\text{C-H vibrations}\)

By analogy with the \(\alpha\)-D(+) Glucose spectrum, the infrared bands deriving from C-H vibrations for all starch samples and their respective assignments are presented in table 6.IX. In this table one can observe that the asymmetric CH stretching in CH\(_2\) (2920-2930 cm\(^{-1}\)) and the CH deformation (1454-1463 cm\(^{-1}\)) and the CH deformation (type II vibration, characteristic of the anomeric form - \(\text{C}_5\)-H, at 850-860 cm\(^{-1}\)) are present in all spectra. The other CH bands appearing in the \(\alpha\)-D(+) Glucose spectrum are also present in some of the starch samples. Potato starch shows the most well-defined spectra among all samples with respect CH vibrations.

(ii) \(-\text{OH Vibrations}\)
Figure 6.20 - Infrared Spectra of: (1) - Potato Amylopectin and (2) - Potato Amylose.
Figure 6.21 - Infrared Spectra of: (1) - Tapioca Starch and (2) - Potato Starch.
Figure 6.22 - Infrared Spectra of: (1) Collamil (Commercial Grade Corn Starch) and (2) Corn Starch.
Figure 6.23 - Infrared Spectra of Corn Starch:
(1) - As in Fig. 6.22 and (2) - New.
TABLE 6.IX - Major C-H Vibrations in the I.R. Spectra of Starches
(Figures 6.20 - 6.23) (*)

<table>
<thead>
<tr>
<th>Starch Sample</th>
<th>asym.</th>
<th>sym.</th>
<th>scissoring</th>
<th>bending</th>
<th>wagging</th>
<th>def str.</th>
<th>C-H Vibrations(cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potato Amylopectin</td>
<td>2923</td>
<td>2817</td>
<td>1454</td>
<td>1593</td>
<td>absent</td>
<td>853</td>
<td></td>
</tr>
<tr>
<td>Potato Amylose</td>
<td>2927</td>
<td>absent</td>
<td>1462</td>
<td>1393</td>
<td>absent</td>
<td>852</td>
<td></td>
</tr>
<tr>
<td>Tapioca Starch</td>
<td>2929</td>
<td>2889</td>
<td>1462</td>
<td>absent</td>
<td>absen</td>
<td>859</td>
<td></td>
</tr>
<tr>
<td>Potato Starch</td>
<td>2923</td>
<td>2895</td>
<td>1462</td>
<td>1385</td>
<td>1290</td>
<td>859</td>
<td></td>
</tr>
<tr>
<td>Collamil(CornStarch)</td>
<td>2930</td>
<td>absent</td>
<td>1460</td>
<td>absent</td>
<td>1300</td>
<td>860</td>
<td></td>
</tr>
<tr>
<td>Corn Starch</td>
<td>2929</td>
<td>absent</td>
<td>1463</td>
<td>1381</td>
<td>absent</td>
<td>857</td>
<td></td>
</tr>
</tbody>
</table>

(*) See TABLE 6.VIII for abbreviations.
Again by analogy with the assignments made for α-D(+) Glucose (table 6.VIII), the major OH bands for all starches are given in the table 6.X. With respect to OH vibrations, the tapioca starch sample is the one showing most of the peaks found in the α-D(+) Glucose spectrum. The in plane OH bending is assigned at the same frequency of the CH₂ scissoring deformation (superimposed). The lower frequency out of plane OH vibrations are present in all starches. At least three peaks are well defined. The peaks at 661cm⁻¹ found in tapioca and potato starch spectra are situated approx. 20cm⁻¹ above the same peak for α-D(+) Glucose. This can be regarded as being caused by the strong intermolecular H-bonding present in the polymers.

(iii) - CO, COH and Ring Vibrations

Table 6.XI gives the assignments for these vibrations for all starches by analogy with α-D(+) Glucose assignments. Some important aspects are presented in Table 6.XI. All starches show type I and type III ring vibrations shifted towards higher and lower wavenumbers, respectively, as compared to α-D(+) Glucose. These shifts have been associated with the type of intermolecular linkages in different polysaccharides (Rao, 1963). In the case of starches, these shifts would be related to α-D(+) (1→4) linkages, as in amylose. Literature reported values (Rao,
TABLE 6.X - Major O-H Vibrations in the I.R. Spectra of Starches
(Figures 6.20 to 6.23)

<table>
<thead>
<tr>
<th>Starch Sample</th>
<th>O-H vibrations (cm(^{-1}))(*)</th>
<th>str.</th>
<th>H-O-H</th>
<th>i.p. bending</th>
<th>o.o.p. bending</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>flexion</td>
<td>(a) (b) (c)</td>
</tr>
<tr>
<td>Potato Amylopectin</td>
<td></td>
<td>3415-3425</td>
<td>1644</td>
<td>1459 abs. abs.</td>
<td>614,551,492</td>
</tr>
<tr>
<td>Potato Amylose</td>
<td></td>
<td>3415-3425</td>
<td>1641</td>
<td>1462 abs. abs.</td>
<td>616,557,484</td>
</tr>
<tr>
<td>Tapioca Starch</td>
<td></td>
<td>3550-3150</td>
<td>1643</td>
<td>1462 1341 abs.</td>
<td>(?)661,609,552,507</td>
</tr>
<tr>
<td>Potato Starch</td>
<td></td>
<td>3600-3200</td>
<td>1640</td>
<td>1462 abs. abs.</td>
<td>(?)661,619,602,553,508</td>
</tr>
<tr>
<td>Collamil (Corn Starch)</td>
<td></td>
<td>3440</td>
<td>1651</td>
<td>1460 abs. abs.</td>
<td>612,550,510</td>
</tr>
<tr>
<td>Corn Starch</td>
<td></td>
<td>3431</td>
<td>1645</td>
<td>1463 abs. abs.</td>
<td>614,551,505</td>
</tr>
</tbody>
</table>

(*) See Table 6.VIII for abbreviations.
TABLE 6.XI - C-O, C-OH and Ring Vibrations in the I.R. Spectra of Starches
(Figures 6.20 to 6.23)

<table>
<thead>
<tr>
<th>Starch Samples</th>
<th>C-O-C</th>
<th>asym. in</th>
<th>COH</th>
<th>CO</th>
<th>Type I</th>
<th>Type III</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>asym.str.</td>
<td>phase ring</td>
<td>str.</td>
<td>str.</td>
<td>ring str.</td>
<td>breathing</td>
</tr>
<tr>
<td>Potato Amylopectin</td>
<td>1163</td>
<td>abs.</td>
<td>shoulder 1043</td>
<td>926</td>
<td>760</td>
<td></td>
</tr>
<tr>
<td>Potato Amylose</td>
<td>1160</td>
<td>abs.</td>
<td>1080</td>
<td>1043</td>
<td>930</td>
<td>760</td>
</tr>
<tr>
<td>Tapioca Starch</td>
<td>1157</td>
<td>abs.</td>
<td>1084</td>
<td>1023, 949</td>
<td>989</td>
<td>736</td>
</tr>
<tr>
<td>Potato Starch</td>
<td>1164,1154</td>
<td>abs.</td>
<td>1098</td>
<td>1038, 930</td>
<td>761</td>
<td></td>
</tr>
<tr>
<td>Collamil(Corn Starch)</td>
<td>1158</td>
<td>abs.</td>
<td>1082</td>
<td>1011</td>
<td>929</td>
<td>764</td>
</tr>
<tr>
<td>Corn Starch</td>
<td>1159</td>
<td>abs.</td>
<td>1078</td>
<td>1016, 928</td>
<td>761</td>
<td></td>
</tr>
</tbody>
</table>

(*) See table 6.VIII for abbreviations.
1963) for the shifted peaks are 930cm\(^{-1}\) for type I vibration and 760cm\(^{-1}\) for type III, in very good agreement with the values given in table 6.XI. The absence of the asymmetric in-phase ring stretching at approx. 1100cm\(^{-1}\) is in agreement with the results of de Araujo (1982) and Khosla (1983). It is in partial agreement with the results of Colombo and Rule (1967). In the latter case, very weak signals were found for some starch samples at 1100cm\(^{-1}\), although this peak was absent in tapioca starch and amylopectin. Being a weak signal located near a strong band (at 1080cm\(^{-1}\)), it may be superimposed on this stronger band.

(iv) - Impurity Related Vibrations

Starches are known to possess different impurities. The presence of such impurities can sometimes be detected by infrared spectoscopy. Colombo and Rule (1967), e.g., reported the presence of protein impurities in starches through a careful analysis of infrared (ATR) spectra. Protein impurities are known to be preferentially associated with the amylose fraction. Other commonly occurring impurities are fatty acids and esterified phosphate groups. In the first case, the presence of COOH group will give rise to very characteristic infrared absorption bands. In the second case, the differentiation is more difficult or even impossible because the frequency range for major P.O.C
vibrations coincides with some of strong starch bands. Table
6.XII presents the tentative assignments of the vibrations
previously left unassigned. An analysis of table 6.XII
demonstrates that of the six starch samples investigated only
"collamil" corn starch did not show impurity related bands.
Earlier infrared studies of de Araujo (1982) also indicated
the absence of impurities in this same reagent. This starch
sample was not used in the experimental work and its infrared
spectrum was recorded for comparison purposes only (in view
of the author's previous experience with this sample).

As expected, potato amylose gave definable protein
related peaks at 1551cm\(^{-1}\) and 1500cm\(^{-1}\). These bands were
absent in potato amylopectin. However, both potato amylose
and amylopectin presented an infrared peak at approx.
1730cm\(^{-1}\) which can be attributed to a carbonyl vibration
(C=O stretching). Protein impurities were also found in the
spectra of potato, corn and tapioca starches. Apparently the
most impure starch is the tapioca sample (commercial grade,
from Thailand). The presence of phosphate groups could not
be ascertained from the recorded spectra. The frequencies
where P-O vibrations are expected to appear coincide with
major vibrations of starch bonds , hence precluding any
conclusive interpretation on this regard. The peak at
1244cm\(^{-1}\) displayed by tapioca starch could have been
assigned to a P = O stretching vibration. However it could
also be assigned to C - O stretching or C - N stretching plus
NH in plane bending. The vibration assigned to adsorbed
TABLE 6.XII - Tentative Assignments of Impurity Related Bands in the I.R. Spectra of Starches (figures 6.20 to 6.23) (*)

<table>
<thead>
<tr>
<th>Starch Samples</th>
<th>Wavenumber(cm⁻¹)</th>
<th>Assignment</th>
<th>Source(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potato Amylopectin</td>
<td>2350</td>
<td>CO₂ str. (gas)</td>
<td>Spurious CO₂ band</td>
</tr>
<tr>
<td></td>
<td>1731</td>
<td>C = O str.</td>
<td>Fatty Acid or Alkyl Ester</td>
</tr>
<tr>
<td>Potato Amylose</td>
<td>1730</td>
<td>C = O str.</td>
<td>&quot; &quot; &quot; &quot; &quot;</td>
</tr>
<tr>
<td></td>
<td>1551</td>
<td>N-H bending</td>
<td>Protein</td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>NH₂ def.</td>
<td>Protein (Amide II)</td>
</tr>
<tr>
<td>Potato Starch</td>
<td>1769 (sh)</td>
<td>C = O asym. str.</td>
<td>Fatty Acid (?)</td>
</tr>
<tr>
<td></td>
<td>1562</td>
<td>NH₂ def.</td>
<td>Protein (Amide II)</td>
</tr>
<tr>
<td></td>
<td>1400</td>
<td>COO⁻ asym. str.</td>
<td>Carb. Acid Dimer</td>
</tr>
<tr>
<td>Collamil (Corn Starch)</td>
<td>707</td>
<td>N-H o.o.p. bend,</td>
<td>Protein</td>
</tr>
<tr>
<td>Corn Starch</td>
<td>1514</td>
<td>NH₂ def.</td>
<td>Protein (Amide II)</td>
</tr>
<tr>
<td>Tapioca Starch</td>
<td>1790</td>
<td>C = O asym. def.</td>
<td>Aliphatic Carb. Acid</td>
</tr>
<tr>
<td></td>
<td>1730</td>
<td>C = O str.</td>
<td>Fatty Acid</td>
</tr>
<tr>
<td></td>
<td>1570</td>
<td>N-H bending</td>
<td>Protein</td>
</tr>
<tr>
<td></td>
<td>1416</td>
<td>COO⁻ asym. str.</td>
<td>Carb. Acid Dimer</td>
</tr>
<tr>
<td></td>
<td>1244</td>
<td>P = O str/C-Ostr, Esterified Phos./C-N str. + N-H</td>
<td>Fatty Acid/ i.p. bending</td>
</tr>
</tbody>
</table>

(*) see TABLE 6.VIII for abbreviations
H$_2$O at ca. 1650 cm$^{-1}$ can also be related to C = 0 stretching in protein impurities. Although the assignment of this vibration to adsorbed H$_2$O is the most probable, one should consider the superimposition of this band by a protein related band. El-Hinnawy et al. (1982) assigned a band at 1650 cm$^{-1}$ to phosphate groups in the infrared spectrum of potato starch. Although this assignment can also be correct, it is this author's opinion that it can not be conclusive.

In summary, infrared spectroscopy applied as a characterization technique for starches was able to provide useful information on the following aspects:

(i) - all samples studied are starches, presenting all major and unique infrared bands of the monomer α-D(+)-Glucose;

(ii) - as expected, different impurities are present in the starches tested. Later in this thesis, this information will be used as support for mechanistic interpretation of the behaviour of apatite/starch systems;

(iii) - the type of the impurities detected in the infrared spectra of the samples is in agreement with data available in the literature.

6.2.2 - Electrophoresis

Although electrokinetic methods are not widely used
for the characterization of starches, they can provide information regarding the state of the starch grain/water interface. The studies described in this section were carried out to show the presence of ionic groups on the surface of starch grains.

Starch grains are known to carry negative surface charge in sea water (Parks, 1975). This charge has been shown to be a function of pH, grain pre-treatment (e.g., lipid extraction) and starch type (Marsh and Waight, 1982). Water-extracted wheat starch (B type) was found to present an iep at pH 3.7. In turn, potato starch was shown to carry a negative surface charge from pH 1.8 to pH 10, regardless of the pre-treatment routine used (Marsh and Waight, 1982).

The nature of the surface charge displayed by non-modified starch (i.e., not transformed into an anionic or cationic polymer by reaction with specific chemical groups), should be related to the presence of ionic impurities. Marsh and Waight (1982) explained the surface charge on wheat B starch as due to the presence of both lipids (phosphate ester, quaternary ammonium groups and free fatty acids) and protein impurities. The positive charge below the iep was related to amino groups on surface lipids and protein. This positive charge could be removed by an EDTA treatment. The negative charge was correlated to both phosphate and carboxylic groups. In the case of potato starch (which did not display an iep in the pH range tested), the negative
charge was considered to be present in a phosphate diester, with $pK_a<2.5$.

Table 6.XIII summarizes the results obtained in the present work. From the results shown in this table, it is clear that all samples displayed a negative surface charge at pH 5.7 in distilled water. Potato amylose and amylopectin had to be ground in an agate mortar and pestle before the measurements (performed in a Zeta Meter). The other samples were submitted to electrophoresis as received, except in the case of ethanol treatment (at room temperature for 60 minutes).

Potato amylose presented the smallest negative absolute E.M. value among the samples. The highest negative absolute value was reached by corn starch. The relatively small negative E.M obtained for amylose and amylopectin as compared to the other samples might be related to the grinding of these samples just prior to electrophoresis. This could have partially altered the positioning of surface impurities of the grains.

The other three samples (viz. potato, tapioca and corn starches) presented similar E.M. values. Corn and potato starches when subjected to the ethanol treatment had their absolute E.M. values reduced by approx. 30%.

If the Helmholtz-Smoluchowski equation is used to convert the obtained E.M. to zeta potential values (see table 6.XIII), these results can then be directly compared to those of Marsh and Waight (1982). These workers also used
TABLE 6.XIII - Microelectrophoretic Mobilities of Starch Grains in Distilled Water (pH 5.7)

<table>
<thead>
<tr>
<th>Starch Sample</th>
<th>Electrophoretic Mobility</th>
<th>Zeta Potential(^{(*)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potato Amylose</td>
<td>-1.20</td>
<td>-16.0</td>
</tr>
<tr>
<td>Potato Amylopectin</td>
<td>-1.15</td>
<td>-15.5</td>
</tr>
<tr>
<td>Potato Starch</td>
<td>-2.10</td>
<td>-28.0</td>
</tr>
<tr>
<td>Tapioca Starch</td>
<td>-2.20</td>
<td>-29.5</td>
</tr>
<tr>
<td>Corn Starch</td>
<td>-2.30</td>
<td>-30.8</td>
</tr>
<tr>
<td>Potato Starch treated with ethanol</td>
<td>-1.50</td>
<td>-20.1</td>
</tr>
<tr>
<td>Corn Starch treated with ethanol</td>
<td>-1.50</td>
<td>-20.1</td>
</tr>
</tbody>
</table>

\(^{(*)}\) - ZETA POTENTIAL(mV)= 13.4 (E.M.)
microelectrophoresis in their studies (their investigation covered the pH range from 2 to 10; this author attempted to make measurements also at pH 10 but the grains of starch used in the present work started to swell rapidly at that pH). In the case of potato starch, Marsh and Waight's result at pH 5.7 was approx. -38mV, ten mV more negative than the result obtained here. Marsh and Waight treated their potato starch sample by ethanol followed by refluxing with CHCl₃/CH₃OH to remove surface lipids. After this treatment their potato starch sample showed a zeta potential of approx. -11mV at pH 5.7. The milder treatment used in the present work reduced the potato starch zeta potential value at the same pH from -28mV to -20.1mV. Although the modification obtained in this work was smaller, it confirms that part of the ionic impurities associated with starches can be removed from its grains. The testwork performed here demonstrates the presence of impurities of ionic nature associated with the starch samples used. These impurities were also detected by the infrared spectroscopy work already discussed.

6.2.3 - Viscometry

Capillary viscometers can be used for the determination of the limiting viscosity number (intrinsic viscosity) of potato amylose solutions. In the present investigation measurements of this property were made in order to provide an insight to the molecular size of the
sample used. Tabulated constants for the Mark Houwink equation for similar systems were used to calculate the molecular weight. There are no available data for amylopectin since the technique is not recommended for measurements on branched polymers (Greenwood, 1964). A few measurements were attempted on starch solutions, but the results obtained were not reliable.

Figure 6.24 depicts the limiting viscosity number (ml/g) obtained from plotting the specific viscosity/concentration ratio against potato amylose solution concentration. This same figure also shows a second alternative way to obtain the limiting viscosity number. The tests were performed at pH 12.3 (KOH) on potato amylose solutions freshly prepared and centrifuged for 10 minutes at 12,000 rpm.

The average limiting viscosity number (taking into consideration the two alternative ways to calculate the intercept for zero concentration) is 139 ml/g. This value is in fair agreement with published values ranging from 140 to 590 ml/g for different amyloses (Greenwood, 1970) at pH 13 and 25°C, and is in very good agreement with the data presented by Khairy et al. (1966) who give 139 ml/g also at 25°C and pH 13. Using the constants compiled by Kurata et al. (1975) for potato amylose (25°C) at 0.15 mol/litre KOH (pH = 13.18) which are:

\[
K = 8.36 \times 10^{-3} \text{ml/g} \quad \text{and}
\]
Figure 6.24 - Determination of the Limiting Viscosity Number of Potato Amylose.
the molecular weight of this sample is then (from the Mark Houwink equation 5.3.7):

\[ M.W = 303,000 \text{ daltons.} \]

This value compares relatively well with the molecular weight of potato amylose presented in table 4.VIII of 490,000, determined by light scattering (Young, 1984) and with the results of Khosla (1983) by ultracentrifugation (320,000 daltons).

6.2.4. - Light Scattering Photometry and Starch Solution Preparation.

The light scattering results presented herein are more concerned with the state of starch aqueous solutions and how these solutions are affected by pH, temperature, ageing and shearing than the actual determination of molecular weight.

The molecular weight of starch fractions has been already discussed in a previous section. It should be clear at this point that molecular weight determinations of starch as a whole have limited significance. Only for the starch fractions (amylose and amylopectin) can one find meaningful data.
The light scattering results to be presented as absolute solution turbidity values were gathered at the following experimental conditions (see Anon. 1970a for details):

(i) - Brice Phoenix Light Scattering photometer equipped with a rectangular quartz cell \((R_w/R_c = 1)\), operating at a wavelength of 546nm (green filter);

(ii) - temperature of 25°C;

(iii) - at least three measurements for each determination of the scatter ratio \((G_s/G_w)\);

(iv) - solutions were centrifuged for 10 minutes at 12,000 rpm prior to the measurements.

To give a "ball park" idea on the relationship between absolute turbididty and molecular weight of starch solutions, a 2.5g/l solution of Dextran A (a bacterial linear polysaccharide) was subjected to study in the photometer. This polysaccharide has a known molecular weight (as given by its supplier) in the range of 200,000 to 250,000 daltons. Its solution at pH 5.5 showed an absolute turbidity of \(1.12 \times 10^{-3}\). Potato amylose, which, according to the results presented in the previous section, has a molecular weight of approximately 300,000 daltons, displayed a turbidity of \(6.51 \times 10^{-3}\) for a solution under similar conditions. Potato amylopectin, which is known to possess a much higher molecular weight, at similar conditions gave an absolute
turbidity 6 times higher than that of potato amylose. According to Forster and Sterman (1956) an absolute turbidity/concentration ratio in the range of 2-4 x 10^{-2} corresponds to a molecular weight of approx. 1 million daltons for amylose. If the Forster and Sterman results are considered valid, the potato amylose solution described above would possess a molecular weight in the neighbourhood of 1 million daltons, considerably larger than the molecular weight obtained by the viscosity measurements previously described. Molecular weight discrepancies of this order, as discussed earlier in the literature review section, are not surprising.

Applying equation 5.3.5 to the light scattering results obtained for potato amylopectin solutions (up to 1.25g/litre) and assuming that $R_{90}$ = absolute turbidity and that $H_1$ can be evaluated from tabulated data $((n-n_0/c)^2 = 0.142 ml/g$, Huglin, 1975); one finds a M.W. of approx. 10 million daltons. This value is probably underestimated in view of other reported values. Even so, it demonstrates that amylose has a much lower molecular weight than amylopectin.

The results used for the calculation described and similar data for tapioca and potato starches are depicted in figure 6.25. Tapioca starch solutions at pH 5.5 show a linear relationship to solution concentration, which is not the case for potato amylopectin and potato starch. Figure 6.26 shows a similar relationship for corn starch at pH 10.

Figure 6.27 shows the effect of ageing for 60 hours
Figure 6.25  - Turbidity of Potato Amylopectin, Potato Starch and Tapioca Starch Solutions as a Function of Solution Concentration.
Figure 6.26 - Turbidity of Corn Starch Solutions.
Figure 6.27 - Effect of Aging on the Turbidity of Tapioca Starch Solutions.
on the turbidities of tapioca starch solutions stored at 2 different temperatures (10 and 35°C). In both cases, turbidity decreased significantly, particularly for the solution stored at the lower temperature. This finding confirms that the rate of retrogradation is increased by lowering the temperature. It also confirms that the deterioration of starch aqueous solutions under normal mineral processing laboratory conditions (not completely aseptic) takes place very rapidly.

Figure 6.28 depicts the effect of temperature on the turbidity of tapioca starch aged for 60 hours at 35°C. Although a small increase of turbidity was achieved by lowering the temperature to 22°C, changing temperatures from 15°C to 35°C had little effect on turbidity. At higher temperatures (close to the gelatinization temperature of tapioca starch) turbidity decreased indicating that the thermal regelatinization of a degraded starch solution does not take place. Retrogradation of starch solutions is generally associated with the amylose fraction which can easily precipitate from solution due to its linear configuration. In fact, amylopectin solutions are much more stable than amylose solutions, (Young, 1984). Young (1984) also states that retrograded amylose is insoluble in water unless it is heated above 124°C. The stability of amylose solutions prepared by alkaline gelatinization is also decreased when the solutions are neutralized (as in the procedure used herein).
Figure 6.28 - Effect of Temperature on the Turbidity of Aged Tapioca Starch Solution.
The next figure (6.29) shows the effect of pH on turbidity of potato amylopectin solutions. Except for the pH range from 11 to 12, the turbidity was independent of pH. In the pH range aforementioned, a peak in turbidity appeared. This can be interpreted as the amylopectin macromolecules increasing their relative size by being more fully extended.

The next two figures (6.30 and 6.31) show the effect of physical modification on the turbidities of corn starch and potato amylopectin, respectively. In the first case, shearing of polymer solution was effected in a Waring Blender for different time spans. For a fairly short shearing time of 0.5 min. there was already a very considerable reduction in the turbidity (54% reduction). For longer shearing times (up to 7 minutes) the turbidity was reduced to 44% of the original value. Shearing of polymer solutions promotes degradation of molecular aggregates by breaking them into smaller pieces. This phenomenon is of extreme importance for both flocculation and flotation systems using polymers. In a very recent investigation by Henderson and Wheatley (1987) sheared polyacrylamide solutions showed reduced performance as flocculants (sheared polymers displayed activities as % of the original settling rate in the range from 19 to 37%, greater values were achieved by more anionic polymers). In another recent investigation by Reis (1987) the depressant effect of an impure corn starch ("gritz") used in iron ore reverse flotation systems was shown to be extremely dependent on the extent of physical (mechanical) modification by
Figure 6.29 - Effect of pH on the Turbidity of Potato Amylopectin Solution.

2.6g/l (ORIGINALLY AT pH-6.63)

\( \Delta \) POTATO AMYLOPECTIN
Figure 6.30 - Effect of Shearing on the Turbidity of Corn Starch Solution.
(shearing performed in a Waring Blender)
Figure 6.31 - Effect of Sonic Treatment on the Turbidity of Potato Amylopectin Solution.
shearing. Under certain optimized shearing conditions both recovery and concentrate grade were found to increase in comparison to non-sheared starch. Similar conclusions were also reached by Khosla (1983).

Figure 6.31 shows another type of physical modification. The solution of potato amylopectin was submitted for 1 minute to different set levels in a sonic dismembrator (these levels are plotted in figure 6.31 as arbitrary sonic level settings of the equipment used). Contrary to shearing, there was a small increase in turbidity for low levels of the sonic effect. Turbidity however, decreased abruptly above a certain level. The small increase in turbidity might be associated with an improved homogenization of the solution when submitted to the low intensity sonic field. The abrupt decrease in turbidity (to 56% of the original value) probably reflects a shearing-like effect.

In summary, testwork characterizing the starch samples used herein, provided the following relevant points:

(i) - infrared spectroscopy was successfully used to characterize all starch samples. It provided information regarding the impurities associated with the starch grains.

(ii) - electrophoretic measurements on aqueous
starch suspensions confirmed the presence of anionic groups on the surface of starch grains;

(iii) - viscosity related experiments were able to provide information on the molecular size of amylose;

(iv) - light scattering photometry was successfully used to yield information on the relative molecular sizes of amylose and amylopectin as well as the effects of pH, temperature, aging and shearing on the properties of aqueous solutions of starches.

6.3. - Interaction Between Starches and Solution Species

6.3.1. - Starches/Surfactants

The reaction between starch and iodine has interested chemists since 1812 (Rundle et al., 1944). Amylose aqueous solutions reacted with iodine display a blue colour, derived from a complex formed between amylose and iodine species. Amylopectin also interacts with iodine in aqueous solutions but the complex formed is less stable, differently coloured (red to purple) and the intensity of the reaction is much smaller (Rundle et al., 1944). Plate A shows the colours developed by reacting potato amylopectin, potato starch and potato amylose solutions with KI/Iodine solutions at neutral
PLATE A - REACTION OF STARCH WITH IODINE

A - AMYLOPECTIN
B - POTATO STARCH
C - AMYLOSE
pH and room temperature (test tubes A, B and C, respectively).

Iodine reaction with starch is a function of pH, temperature, concentration and presence of foreign solutes. It is well accepted that iodine molecules and ions become situated in the core of helically oriented amylose molecules (Greenwood, 1970). In turn, amylopectin binds much less iodine than amylose. It has been suggested that the low binding power of amylopectin is related to the large number of branching points in the amylopectin molecules. This would simply disrupt possible helix formation (Greenwood, 1970). In both cases however, a complete understanding of the mechanisms involved is still lacking.

The conformation of these two polymeric molecules in solution has considerable interest regarding their interaction with minerals. For instance, random coil and extended coil conformations will probably increase the flocculating power of the polymers, while the helix conformation should decrease it. Specifically in the case of amylose there are 3 different proposed models for the conformation of this macromolecule in aqueous solutions (Senior and Hamori, 1973). They are: (i) the tight-helix model of Hollo-Szejtli; (ii) the random coil model of Banks-Greenwood; and (iii) the extended coil model of Senior-Hamori. There is one fundamental aspect concerning the models and interaction of amylose with iodine that should be emphasized. If the first model above is correct, iodine
aqueous species react with amylose by occupying an already existing space inside the helical structure. If either of the other two models is correct, iodine species create the helical structure by reacting with amylose. Senior and Hamori (1973) presented intrinsic viscosity studies that contradict partially Hollo-Szejtli's model. Their extended helix model incorporates aspects of the other two proposed models. Amylose macromolecules would possess loose helical portions (not tightly packed) joined together by random coil sections. The formation of the amylose iodine complex according to the Senior-Hamori model can be envisaged as resulting from the entrapment of iodine species by the contraction of helical regions of the macromolecule into tight helices ("V" amylose). This latter aspect is important for the understanding of how surfactants interact with starch molecules as will become clear later in this section.

The interaction between surfactants and starches has been an object of study for some years, especially in the food industry (Takagi and Isemura, 1960; Kim and Robinson, 1979; Bhide et al., 1981; and Bulpin et al. 1982). Most researchers agree that the loss of the characteristic blue colour of the amylose/iodine complex in surfactant solutions results from surfactant species occupying part of the helical cavity that otherwise would be filled by iodine.

Figure 6.32 shows the ultraviolet (UV) - visible (vis.) absorption spectrum for an Iodine/KI aqueous solution at pH 6, containing $1.92 \times 10^{-3}$ mol/dm$^3$KI and $4 \times 10^{-5}$
Figure 6.32 - Ultraviolet(UV)- Visible (Vis.) Spectrum of KI/Iodine Aqueous Solution

(1.92 x 10^{-3} \text{mol/l KI and 4 x 10^{-5} mol/l Iodine}).
mol/dm³ Iodine. The spectrum was obtained in a quartz cell with 1.0 cm of path length. The two absorption peaks at approx. 250 and 350 nm are both related to the yellow iodine/KI solution.

Figure 6.33 (a and b) depicts the UV-vis. spectra of potato amylose and amylopectin solutions (25 mg/litre, pH 6) in the presence of KI/Iodine. This figure clearly shows the different interaction between amylose and amylopectin with iodine. The maximum absorbance for amylose is situated at approx. 600 nm. In turn, the absorbance maximum for amylopectin is located at 550 nm and has a smaller intensity. The positions of the peaks are in good agreement with the data of Bhide et al. (1981). Another feature in figure 6.33 a and b is the absorbance values for residual iodine. It is clear from these values that amylose binds much more iodine than amylopectin.

In figure 6.34, the position of the two absorption maxima is more closely compared. In this case the amount of iodine/KI was doubled for amylopectin. This figure shows more clearly the shift towards lower wavelength occurring for the amylopectin solution.

Figures 6.35 (a and b) and 6.36 depict the effect of pH on amylose and amylopectin. At pH 10, the conformation of the macromolecules is probably different from that at neutral pH. This is reflected by the decrease in intensity of the absorption peaks in both cases. Under acidic conditions, how
Figure 6.33 - UV-Vis. Spectra of (a) Potato Amylose and (b) Potato Amylopectin.
Figure 6.34 - Determination of Absorption Maxima in the UV-Vis. Spectra of Potato Amylose and Potato Amylopectin in the Presence of Iodine.
Figure 6.35 - Effect of pH on the UV-Vis. Spectra of (a) Potato Amylose and (b) Potato Amylopectin.
Figure 6.36 - UV-Vis. Spectrum of Potato Amylose at pH 1.5 in the Presence of Iodine.
tighter helix conformation, as shown by the increase in intensity of the absorption maximum at 600nm. An alternative explanation for the phenomena described resides in the iodine solution species, which themselves are a function of pH. Blanks that were run at pH 10 did not indicate, however, any considerable decrease in absorption maxima related to iodine.

Figure 6.37 shows the absorption spectra for Na Oleate and Dodecylamine Hydrochloride (DDAHCl) solutions both at concentrations of $5 \times 10^{-5}$ mol/litre (pH6) in the presence of iodine/KI. There is no peak for either surfactant in the wavelength range covered by the spectra (800-250nm). Nevertheless, this figure shows that the cationic surfactant interacted with the iodine solution, reducing the intensity of the first absorption maximum related to iodine.

Figure 6.38 (a and b) depicts the effect of Na Oleate ($5 \times 10^{-5}$mol/dm$^3$) on the spectra of 25 mg/litre amylose/iodine solutions at pH 6 and pH 10. In the first case (fig. 6.38a) there is a considerable reduction in peak intensity accompanied by a shift towards lower wavelengths. At pH 10 (fig.6.38b) the long wavelength peak disappears completely. Figure 6.39 shows a similar situation at pH 3.5.

The next figure (6.40) shows the effect of DDAHCl ($5 \times 10^{-5}$mol/dm$^3$). Curves 1 and 3 represent amylose solutions at pH 6 and 10, respectively in the absence of the surfactant. Curves 2 and 4 resulted from the addition of DDAHCl to the system, also at pH 6 and pH 10, respectively.
Figure 6.37 - UV-Vis. Spectra of Na Oleate and Dodecylamine Hydrochloride (DDAHCl) in the Presence of Iodine.
Figure 6.38 - Effect of pH on the UV-Vis. Spectra of Potato Amylose in the Presence of Iodine and Na Oleate (a)-pH6 and (b)-pH10.
Figure 6.39 - Effect of Na Oleate on the UV-Vis. Spectrum of Potato Amylose at pH 3.5 in the Presence of Iodine.
Figure 6.40 - Effect of DDAHCl on the UV-Vis. Spectra of Potato Amylose in the Presence of Iodine:

1 - Potato Amylose at pH6
2 - Potato Amylose/DDAHCl at pH6
3 - Potato Amylose at pH10
4 - Potato Amylose/DDAHCl at pH10.
Figure 6.41 depicts the same situation at pH 3. As in the case of Na Oleate, the effect of DDAHCl was to decrease the intensity of the amylose/iodine peaks, accompanied by a blue shift.

According to Bhide and co-workers (1981), the order of addition of the three reagents (iodine/KI, amylose and surfactant) is important to the final outcome. In their testwork (as in the present testwork) the surfactant solutions were added to the starch solutions prior to the addition of the iodine/KI solution. Bhide et al. found that this sequence of mixing promoted the largest effect in terms of decreasing the intensity of the amylose/iodine peaks. It seems that if iodine is allowed to interact first, only a small portion of its molecules are exchanged by surfactants species.

In contrast to the results obtained in the present testwork and those of Bhide et al.(1981), Kim and Robinson (1979) did not observe a large blue shift in their absorption spectra of amylose/iodine in the presence of polyoxethlene sorbitan monostearate. They did observe however, similar decreases in peak intensities to those obtained here.

Bhide et al.(1981) found that the effect of surfactants on the amylopectin/iodine UV - vis. spectrum is less pronounced than in the case of amylose. Figure 6.42 (a and b) shows the effect of Na Oleate (at pH 6 and pH 10) and DDAHCl (at pH 6) on the absorption spectra of amylopectin/iodine. The concentration of KI/Iodine is twice as much as
Figure 6.41 - Effect of DDAHCl on the UV-Vis. Spectrum of Potato Amylose at pH 3 in the Presence of Iodine.
Figure 6.42 - Effect of (a) Na Oleate and (b) DDAHCl on the UV-Vis. Spectra of Potato Amylopectin in the Presence of Iodine.
that used in the amylose spectra. The spectra obtained present a relatively small decrease in peak intensity in all cases, if these spectra are compared to those of amylose. No shift in the peak position was detected, again in agreement with the results of Bhide et al. (1981).

The same reasoning used earlier to justify the low iodine binding capacity for amylopectin, can be also used to explain the smaller changes encountered in amylopectin/iodine spectra. The absence of significant changes in the spectra can not be used as proof or evidence indicating low levels of interaction however. A more detailed investigation would be necessary to clarify the possible ways of interaction between giant amylopectin molecules and surfactants. Such an investigation is outside the scope of the present work.

Interpretation of the available data and literature led to the following conclusions:

(i) - amylose interacts with anionic surfactants by entrapping their aqueous species into the helical cavity of the macromolecules;

(ii) - reduction of intrinsic viscosity reported by Kim and Robinson (1979) for amylose-surfactant solutions is related to conformational changes that the macromolecules undergo in the presence of surfactants;

(iii) - the shift towards lower wavelengths might be
associated with the breakage of polyiodine resonating chains inside the helical cavity of amylose, caused by the presence of surfactant species;

(iv) - the studies of Takagi and Isemura (1961) indicated that if the surfactant concentration was increased above its CMC, no more changes were observed in the UV - vis. spectrum of the amylose/iodine complex. This suggests that individual surfactant species are concerned with the transformation of the helical complex;

(v) - Davies et al. (1980) presented evidence for the active participation of starch fatty acid in the high temperature (>60°C) retrogradation of amylose. They showed that many surfactants (mostly anionic) yielded amylose crystals of different shapes upon retrogradation.

(vi) - Robb (1981) citing original work by Fisherman and Miller (1980) states that cationic surfactants also interact with starch fractions. A quaternary ammonium salt ($C_{16}H_{33}N$ Methyl$_3$Br) precipitated both amylose and amylopectin, the latter being more effectively precipitated at high pH. While anionic surfactants are reported
to fit into the helical structure of amylose, cationic surfactants might not be able to be accommodated due to the bulkiness of their head groups.

(vii) - in conclusion, starch fractions interact with surfactants in the absence of mineral surfaces. In a flotation system, addition of modifiers (starches for example) generally precede the addition of collectors (surfactants). It is then probable that the interactions such as those just discussed will predominantly take place at the mineral surfaces. Although the place where these interactions occur should not interfere with their existence, one should always keep in mind the different energetic and entropic environment of interfaces. In this way, the interactions can be either enhanced or diminished in their degree.

6.3.2 - Starches/Ca Aqueous Species

To investigate the interaction between starches and Ca aqueous species, a different experimental approach was pursued. Attempts to utilize UV - vis spectra of starch fractions in the presence of iodine and Ca species were unsuccessful. An approach similar to that of Khosla (1983),
Khosla and Biswas (1984) and Cross et al. (1985), which involves the measurement of the depression of solution electrical conductivities (after mixing starch and Ca solutions) was found appropriate. The basic principles of this approach have already been discussed (section 5.3.6).

Figure 6.43 shows the relationship between solution conductivity and potato amylopectin concentration in the presence and absence of a Ca chloride solution (2 x 10^{-3} mol/litre). Figures 6.44 and 6.45 show similar results for potato amylose and potato starch, respectively. The lowest curve represents the experimentally measured conductivity of the starch solution in question. The intermediate curve represents the experimentally measured conductivity obtained by adding 2 x 10^{-3} mol/litre of CaCl_2 to the starch solution. The top curve represents the arithmetic sum of the individual solution conductivities. In the absence of interaction the intermediate and top curves would be coincident.

A closer look at the data reveals that the % decrease in the measured conductivity in relation to that expected by the addition rule presented the following general trends:

(i) - in general, the % decrease diminishes as the concentration is increased (e.g. 19% at 25 mg/litre of potato amylose in contrast to 14% at 228 mg/litre; 17% at 25 mg/litre of
Figure 6.43 - Solution Conductivity of Potato Amylopectin in the Presence and Absence of Calcium Chloride.
Figure 6.44 - Solution Conductivity of Potato Amylose in the Presence and Absence of Calcium Chloride.
Figure 6.45 - Solution Conductivity of Potato Starch in the Presence and Absence of Calcium Chloride.
potato amylopectin in contrast to 11% at 228 mg/litre; 18% at 61 mg/litre of potato starch in contrast to 11% at 268 mg/litre; all data for pH 10.2)

(ii) - lowering the pH from 10.2 to 6 in the case of potato starch decreased the difference obtained between the experimental and the arithmetic sum value for no interaction (maximum % decrease occurred at 217 mg/litre of potato starch and measured 6.3%)

(iii) - in all cases the experimental value obtained for the mixture of starch and Ca solutions was smaller than the no interaction arithmetic sum value. This particularly contradicts the results obtained by Khosla (1983). Khosla's experimental data show a small decrease only in the case amylose/Ca at 150 mg/litre of amylose and 1 x 10^{-3} mol/litre of amylose and 1 x 10^{-3} mol/litre Ca(II). For lower amylose concentrations as well as for amylopectin, the percentage discrepancy was either nil or a small positive value (maximum of 2.3%). Khosla did not mention the pH conditions of his tests. Nevertheless, Cross and co-workers' (1985) experimental data show only depression in the conductivities for various
carbohydrate systems.

Table 6.XIV summarizes the results obtained for tapioca and corn starches also at pH 10.2. In both cases a large % decrease was observed (approx. 25% for tapioca starch and 30% for corn starch).

Most studies on the ability of starches to bind metallic ions are related to the field of food technology (Cross et al., 1985; Kroll, 1984; Sukan et al., 1979; Hood and O'Shea, 1977). According to Cross and co-workers the complexing of metallic ions by both low and high molecular weight carbohydrates is well established and can be demonstrated by depression of conductivity among other techniques. Interesting results were obtained by Sukan et al.(1979) in their work on the Ca binding capacity of potato and corn starches. The more relevant conclusions from their work were:

(i) - Ca binding capacity decreased as the pH was decreased from 7.0 to 4.0 for both starches.

(ii) - Maximum Ca binding values (as %) were 33% for non-treated potato starch followed by 24% for non-treated corn starch.

(iii) - For 1, 4 dioxan extracted starches (used to remove lipids and esterified phosphorus) the amount of Ca bound was reduced from 16% to 18%.
<table>
<thead>
<tr>
<th>Starch Type</th>
<th>Starch/Conc.</th>
<th>Conductivity (micromho)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/litre</td>
<td>Starch alone</td>
<td>mixture</td>
</tr>
<tr>
<td>Tapioca</td>
<td>50</td>
<td>450</td>
<td>875</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>600</td>
<td>975</td>
</tr>
<tr>
<td>Corn</td>
<td>50</td>
<td>950</td>
<td>1150</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>1050</td>
<td>1125</td>
</tr>
</tbody>
</table>
Hood and O'Shea's (1977) results are also relevant. They also found that the Ca binding capacity of tapioca, corn and waxymaize starches were also affected by pH in a similar way as the results of Sukan et al. The order of relative decrease in binding capacity among the 3 samples used was as follows: tapioca > corn > waxymaize starches.

All studies available seem to indicate that the binding of Ca (and other metallic ions) by starches has both nonionic and ionic components (Sukan et al., 1979; Hood and O'Shea, 1977). The presence of esterified phosphorus and other ionic impurities appears to be important to the Ca binding ability of starches.

6.4 - Adsorption of Starches onto Mineral Surfaces

6.4.1 - Preliminary Work

The preliminary adsorption work was designed to show qualitatively (and pictorially) the interaction between starches and mineral surfaces. This test programme was based upon the well established reaction known to occur between starch and iodine (already discussed). Using the colour developed by this reaction, it was possible to show photographically conditions for adsorption and non-adsorption of starches onto two different mineral surfaces, namely silica (Min-U-Sil 5) and hydroxyapatite (Tribasic Calcium Phosphate C-127, Fisher). These two powders were used instead of quartz and fluorapatite because of their high specific
surface areas which made the visual impact of the colour photographs greater. These photographs are shown in plates B, C, D and E.

Plate B shows 10 test tubes (a to j). The caption in plate B describes in detail the test conditions and the compositions of each solution. Test tubes a and b show silica and hydroxyapatite, respectively, subjected to a solution of potato starch. No iodine was added in these two test tubes. Plate C shows a close-up view of the settled solids. It is clear that the two solids settled under different conditions. The height of the sediment is much smaller for silica than for hydroxyapatite, indicating that the first solid settled to a compacted bed (i.e. it was dispersed), and the latter settled to much lighter bed, typical of flocculated sediment. In the absence of starch both solids settled to compact sediments, similar to the silica sediment in the presence of starch.

Test tubes c and d in plate B show exactly the same situation encountered for test tubes a and b but in the presence of iodine. Plate D shows again close-up detail of these sediments. Adsorption of potato starch onto hydroxyapatite in the presence of iodine caused a remarkable change in the colour of the settled powder (test tube d).

Under the conditions of this test, as indicated by the total absence of any colouration in the supernatant solution in test tube d, there was 100% adsorption of starch on the powder. Test tube c, containing silica, depicts an opposite
PLATE B - INTERACTION OF POTATO STARCH, AMYLOSE AND AMYLOPECTIN WITH SILICA AND HYDROXYAPATITE.

CONDITIONS: SETTLING TIME = 24 HRS / pH = 10

POLYMER = 60 mg / 1.4 ml of KI/IODINE → [KI] = 0.24 mol / l, [I₂] = 0.005 mol / l

TEST TUBES

A - SILICA + POTATO STARCH (no iodine)
B - HYDROXYAPATITE + POT. STARCH (no iodine)
C - AS IN "A" (iodine added)
D - AS IN "B" (iodine added)
E - SILICA + AMYLOPECTIN (iodine added)
F - HYDROXYAPATITE + AMYLOPECTIN (iodine added)
G - SILICA + AMYLOSE (iodine added)
H - HYDROXYAPATITE + AMYLOSE (iodine added)
I - POTATO AMYLOSE (iodine added)
J - POTATO AMYLOPECTIN (iodine added)
PLATE C - DETAILS OF THE SEDIMENTS IN TEST TUBES "A" AND "B" SHOWN IN PLATE B

A - SILICA + POTATO STARCH
B - HYDROXYAPATITE + POTATO STARCH
PLATE D- DETAILS OF THE SEDIMENTS IN TEST TUBES "C" AND "D" SHOWN IN PLATE B

(THIRD TUBE CONTAINS POT.STARCH + IODINE)

C - SILICA + POTATO STARCH (Iodine added)
D - HYDROXYAPATITE + POT.STARCH (Iodine added)
PLATE E- DETAILS OF THE SEDIMENTS IN TEST TUBES "G" AND "H" SHOWN IN PLATE B

G - SILICA + AMYLOSE (iodine added)
H - HYDROXYPATITE + AMYLOSE (iodine added)
situation. There is no visible change in the colour of the sediment but, in turn, the supernatant solution is blue, hence indicating a non-adsorption condition.

Test tubes e and f in plate B show the same situation for potato amylopectin. For potato amylose, test tubes g and h again show similar results. Plate E also shows a close-up view of the sediments in test tubes g and h from plate B.

This introductory section to the adsorption test programme discussed later, demonstrates some important features concerning the adsorption of starches onto mineral surfaces:

(i) starch adsorbs preferentially onto hydroxyapatite as compared to silica surfaces (under the conditions tested);

(ii) the adsorption of starch on hydroxyapatite promotes its flocculation. Although the photographs show only the final result after 24 hours, the complete settling of hydroxyapatite particles in the test tube took only a few minutes;
(iii) - both amylose and amylopectin adsorb on hydroxyapatite and promote flocculation.

6.4.2 - Selection of the Analytical Procedure

For the quantitative estimation of the adsorption of starches, two different analytical procedures are available:

(i) - starch-iodine method (Cooke et al., 1952, Hanna, 1973; Whistler and Daniel, 1983)

(ii) - phenol-sulphuric acid method for carbohydrates (Dubois et al., 1956; Khosla, 1983; Steenberg and Harris, 1984; Solari et al., 1986)

Both methods rely on colorimetric measurements. The first method has some advantages regarding handling and speed. The second method is probably more precise since it is free from interferences caused by lipids.

Since the adsorption test programme envisaged in the present work did not involve the co-adsorption of surfactants
and in view of the results obtained in preliminary tests described in the next paragraph, the first method was chosen. Details on the calibration curves used for each starch sample tested are given in Appendix III.

Comparative adsorption tests involving both analytical procedures are presented in table 6.XV. These results demonstrated that, within the experimental error, both methods gave equivalent results.

6.4.3 - Adsorption Kinetics

Adsorption of macromolecules is a slower process than the adsorption of low molecular weight substances. This is particularly true if the molecular weight distribution is wide (Fleer and Lyklema, 1983), as in the case of starches.

Most research work available in the literature on the adsorption of starch on different mineral systems points to 1 hour equilibration times to ensure complete adsorption (Balajee and Iwasaki, 1969; Hanna, 1973; Steenberg, 1982; Khosla, 1983; Khosla and Biswas, 1984; and Steenberg and Harris, 1984).

Figure 6.46 shows the effect of time on the adsorption of potato starch on fluorapatite at pH 10.1. The initial concentration of starch was 50mg/litre and all data points were obtained independently. Equilibrium (or
TABLE 6.XV - Comparison of Analytical Procedures Commonly Used for the Determination of Starch Concentrations in Aqueous Solutions (adsorbate-hydroxapatite(*)) at pH 10, 1 hour equilibration time).

<table>
<thead>
<tr>
<th>Starch Sample</th>
<th>Initial Concentration (mg/l)</th>
<th>Residual Concentration (as % of the initial conc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potato Amylose</td>
<td>20</td>
<td>5.2</td>
</tr>
<tr>
<td>Potato Amylopectin</td>
<td>20</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>3.7</td>
</tr>
<tr>
<td>Potato Starch</td>
<td>50</td>
<td>5.3</td>
</tr>
</tbody>
</table>

(*) The specific surface area of this sample is much higher than that of the -38 µm fluorapatite sample used for most of the adsorption testwork.
Figure 6.46 - Adsorption Kinetics of Potato Starch on Fluorapatite.
residual) starch concentrations are also shown in the same diagram. From the analysis of the data presented, an equilibration time of approx. 10 minutes is sufficient to attain maximum adsorption. Without any further testing, an equilibration time of 1 hour was considered long enough to represent adsorption at equilibrium.

6.4.4 - Equilibrium Adsorption Tests

6.4.4.1 - Adsorption of Starches in the Absence of Other Solutes.

Figure 6.47 shows the adsorption(*) isotherms (23°C) obtained for the adsorption of potato starch, amylose and amylopectin on fluorapatite at pH 10.1. All three isotherms present a similar shape, and a plateau region is achieved in all cases.

The isotherm shape encountered, especially for the case of potato amylopectin, is what is known in the technical literature as a high-affinity isotherm (Lipatov and Sergeeva, 1974; Fleer and Lyklema, 1983). Most polymers adsorbed onto solids display such a high-affinity isotherm, characterized by the fact that in the initial part of the isotherm, at

(*) - Adsorption is expressed in mg per m² of available surface. In systems such as the ones studied here where the adsorbent has a wide molecular weight distribution these adsorption isotherms should be viewed more as "abstraction" curves, as suggested by Balajee and Iwasaki (1969).
Figure 6.47 - Adsorption Isotherms of Potato Starch, Amylose and Amylopectin on Fluorapatite.
undetectably low concentration, the adsorbed amount rises steeply, whereas at higher concentrations it reaches a (pseudo) plateau (Fleer and Lyklema, 1983). Similarly shaped isotherms can be found in the literature for the adsorption of starches onto certain mineral surfaces (Balajee and Iwasaki, 1969; Hanna, 1973).

Figure 6.47 also shows the potato amylopectin plateau is higher than that observed for potato starch or amylose (the latter being the lowest). For the concentration range covered, there was no sign of an S-shaped isotherm similar to that found by Steenberg (1982) and Steenberg and Harris (1984) for the adsorption of a modified potato starch on apatite at pH 7.0. These researchers obtained an isotherm characterized by a plateau region situated between 10 and 40 mg/l (equilibrium concentration), followed by a second steep rise in the amount adsorbed above 50mg/l and up to 75mg/l (equilibrium concentrations). They did not offer any explanation for their findings.

Khosla (1983) found differently shaped isotherms in his adsorption studies for starch, amylopectin and amylose on both hematite and calcite. In some instances the isotherms encountered by Khosla resemble those shown in figure 6.47. For amylopectin and amylose adsorbed on calcite, he obtained isotherms of a very unusual shape, not characteristic of the adsorption of polymers on mineral surfaces.

In an earlier work, Somasundaran (1969) found isotherms without a plateau region for his studies on the
adsorption of starch on calcite. His isotherms however bear more resemblance to the ones shown in figure 6.47 than to those found by Khosla (1983) and Steenberg (1982).

Figure 6.48 shows the adsorption isotherm for tapioca starch on fluorapatite, also at pH 10.1. It is similar in shape to the amylopectin isotherm shown in figure 6.47 but the maximum adsorption density (0.91 mg/m²) is smaller than that achieved by amylopectin (0.99 mg/m²). It is however higher than the 0.85 mg/m² reached by potato starch (fig. 6.47).

The differences both in shape and adsorption maxima can be related to the relative molecular weights of the polymers. It can also be related however to a higher affinity displayed by tapioca starch and amylopectin for the surface.

Somasundaran (1969) was the first to indicate that Ca ionic species can play a role in the adsorption of starches on Ca-bearing surfaces. The affinity between starch and Ca has already been subject to experimental work in the present thesis. The depression in solution conductivities observed when Ca and starch solutions are mixed together has been interpreted as evidence for the formation of Ca/starch complexes.

Figure 6.49 shows an extra piece of evidence in favour of Ca playing a major role in the adsorption of starch on apatite. In this figure the Ca residual concentration is plotted as a function of starch equilibrium concentration.
Figure 6.48 - Adsorption Isotherm of Tapioca Starch on Fluorapatite.
Figure 6.49 - Residual Calcium Concentration upon Adsorption of Potato and Tapioca Starches on Fluorapatite.
for tests involving the adsorption of potato and tapioca starches. At low equilibrium concentrations, where the plateau regions in both adsorption isotherms had not yet been reached, there was a decrease in the amounts of Ca left in solution. As the residual concentration approached plateau values in the isotherms, the amount of Ca in solution increased.

Data of Somasundaran (1969) for the starch/calcite system are similar to those shown in Fig. 6.49 although his do not show the initial decrease in Ca concentration. In any case, the participation of Ca ionic species in the adsorption mechanism is evident.

One possible interpretation for the data presented in figure 6.49 is that at low equilibrium concentrations starch complexes Ca ions at the interface. As the concentration is increased, the equilibrium condition is re-established. At pH 10.1 the surface of fluorapatite is negatively charged, indicating that the majority of sites on the surface are anionic in character. Calcium ionic species at this pH are present only in the form of Ca(II) cations. They probably populate the electrical double layer together with H^+ ions, as counter-ions. At low equilibrium (residual) starch concentrations, most of the polymer is adsorbed. This might be the reason for the lowering of Ca residual concentration in the bulk solution. Starch macromolecules can decrease the surface solubility by blocking many of the Ca(II) surface sites available. As the
adsorption proceeds to higher amounts adsorbed, hydrogen bonding among the many adsorbed macromolecules can provide an extra driving force. Equilibrium conditions would then be re-established for Ca ions in solutions.

Figure 6.50 shows the pH dependence for the adsorption of tapioca starch on fluorapatite. Maximum adsorption is found in the pH range from 10 to 11. Most studies on the adsorption of starches on minerals show a slight decrease in adsorption as the pH is increased from 7 to 10, followed by a more drastic decrease at pH values above 11 (Somasundaran, 1969; Balajee and Iwasaki, 1969). Khosla (1983) observed decreased adsorption for starch on hematite as the pH was increased from 7 to 10, but did not observe any effect in the case of calcite (contrary to the data of Somasundaran, 1969).

The experimental facts depicted in figure 6.50, although contrary to most accepted theories of a diminishing adsorption as the pH is increased (as a result of electrostatic repulsion), provide new evidence for the proposed adsorption mechanism involving Ca ions. At pH values close to the samples' pzc, minimum solubility is expected. Therefore, if more Ca ions become available as the pH is raised above the pzc(pH) adsorption can indeed increase as well. The eventual decrease in adsorption is experienced at a much higher pH. Electrostatic repulsion might then be considered relevant to the overall adsorption mechanism. Steenberg (1982) also found increased adsorption as pH was
Figure 6.50 - Effect of pH on the Adsorption of Tapioca Starch on Fluorapatite.
raised from 7 to 11. She did not comment on this result.

6.4.4.2 - Effect of Ca Ions(*)

As demonstrated above, Ca species play an important role in the adsorption of starches on fluorapatite. Tests involving the external addition of Ca ions were thereby considered important for the understanding of the role of such ions in the adsorption of starches.

Figure 6.51 shows the adsorption of potato amylopectin on fluorapatite in the presence of Ca ions (the adsorption isotherm in the absence of Ca ions was replotted from Figure 6.47). The isotherms shown in figure 6.51 demonstrate that Ca ions were capable of increasing the level of the adsorption plateau, by approximately 40%. Figure 6.52 shows a similar situation for the adsorption of tapioca starch (now in the presence of a concentration of Ca ions ten times higher). Maximum adsorption was increased by more than 60%. The data presented in both figures confirm the activating effect of Ca ions on the adsorption of starches.

To investigate further the involvement and the role of Ca ions in the adsorption of starches onto mineral surfaces, some adsorption isotherms were obtained for quartz. Firstly, figure 6.53 shows the adsorption of tapioca and

(*) - Care was exerted during the analyses of starch residual concentrations in the presence of Ca ions (see appendix III).
Figure 6.51 - Effect of Ca Ionic Species on the Adsorption of Potato Amylopectin on Fluorapatite.
Figure 6.52 - Effect of Ca Ionic Species on the Adsorption of Tapioca Starch on Fluorapatite.
Figure 6.53 - Adsorption Isotherms of Tapioca and Potato Starches on Quartz.
potato starches on quartz at pH 10.1. The adsorption isotherms for fluorapatite obtained earlier are also replotted in fig. 6.53 for comparison purposes. The shape of the isotherms obtained for quartz is different from that of fluorapatite. Also, the amount adsorbed on quartz is very much smaller. This result is not surprising if one recalls the preliminary adsorption testwork (discussed in section 6.4.1).

Figure 6.54 shows the adsorption of tapioca starch on quartz with two levels of Ca ion additions. In both cases, there is an increase in adsorption on quartz in the presence of Ca ions. For the highest level of addition, the isotherm displays high adsorption densities, particularly at high residual concentrations of starch.

The data in figures 6.53 and 6.54 manifest the importance of Ca ions in the adsorption of starches. While a diminished electrostatic repulsion, caused by the presence of Ca ions, might be largely responsible for the increased adsorption, one should also consider the considerable evidence pointing to Ca / starch specific interactions. Quartz particles in the presence of \(1 \times 10^{-3}\)mol/litre Ca ions possess a surface charge less negative than that of fluorapatite in the absence of such ions at pH 10.1 (see figures 6.9 and 6.13). Considering both surfaces equally capable of hydrogen bonding, if electrostatic forces were the only other component to the overall adsorption mechanism, quartz would display higher adsorption than fluorapatite.
Figure 6.54 - Effect of Ca Ionic Species on the Adsorption of Tapioca Starch on Quartz.
The shape of the isotherms does not confirm such a postulate since adsorption isotherms on fluorapatite all depicted a very sharp increase in the amount adsorbed for very low residual concentrations. That is not the case for quartz, even in the presence of Ca ions. Hence, there must exist forces other than electrostatic and hydrogen bonding, contributing to the overall adsorption mechanism. Most probably, the presence of Ca sites in the surface together with Ca ions at the interface, are necessary to promote high-affinity adsorption isotherms for starch on minerals. This would explain the very noticeable preferential adsorption of starch on fluorapatite as compared to quartz. This observation is in complete agreement with the well established role of starch as a selective flocculant for phosphate ores with siliceous gangue (Coelho, 1984 and de Araujo et al., 1986).

Data showing the increased adsorption of starch on quartz in the presence of Ca species should also be emphasized. In a mineral pulp, the presence of ubiquitous ions is a constant. Ca ionic species present in such systems, either from more soluble minerals or externally added (hard water source) can cause serious selectivity problems. The presence of Ca (and other ions) might represent one of the reasons for the necessity of using dispersants. They would also control the total amount of dissolved cations, which could promote a loss in selectivity in the adsorption of starch in real mineral pulps.
In summary, the adsorption of starches on fluorapatite is dependent on the pH, starch molecular weight and presence of Ca species. The overall adsorption mechanism is, most probably, of a chemical nature, involving the formation of Ca/starch complexes. The formation of these complexes is likely to be dependent on the presence of ionic groups on starch macromolecules. Examples are the well known impurities like esterified phosphate and carboxylic groups. It is also possible however that complexes are formed through a non-ionic interaction between starch and Ca, as proposed by some researchers (Sukan et al., 1979).

The extent of adsorption of starch onto quartz surfaces in the absence of foreign Ca species is much smaller than on fluorapatite. Nevertheless, in the presence of Ca ions, starch also adsorbs on the modified quartz surfaces. This can cause considerable problems in the action of starch as a selective flocculant for fluorapatite/quartz systems. It is one reason for the need for dispersants to promote a selective action of starches.

6.5 - Flocculation Studies: Starch as a Flocculant.

6.5.1 - Preliminary Tests

Preliminary flocculation tests were set up to obtain conditions (pH and starch dosages) for the more quantitative work described in sections 6.5.2 and 6.5.3.
This test programme was carried out using the sedimentation tube described earlier (section 5.3.9). Two mineral samples were used, namely kaolinite and fluorapatite (overflow from the beaker decantation tests). The degree of flocculation \((F_{h,t})\) was calculated according to the equation 5.3.10.

Figure 6.55 shows the degree of flocculation for fluorapatite and kaolinite (single mineral tests) in the presence of potato starch, amylopectin and amylose at pH 10. The first striking fact shown in Figure 6.55 is that the degrees of flocculation of kaolinite are much smaller than those obtained for fluorapatite, irrespective of the starch used. The second observation deals with the relative flocculation power of the three starch solutions. Amylopectin exhibits the highest flocculation activity among the three starches, closely followed by potato starch. Potato amylose was also able to flocculate fluorapatite but higher degrees of flocculation were reached only at higher polymer dosages.

Figure 6.56 shows the effect of tapioca starch on the flocculation of fluorapatite and kaolinite at pH 10. The degrees of flocculation were again much higher for fluorapatite than for kaolinite. At approximately 10mg/l of tapioca starch, there was a peak in the flocculation degree. Tapioca starch also presented a more noticeable re-stabilization of the suspension at high dosages as compared to potato starch, amylopectin and amylose.
Figure 6.55 - Degree of Flocculation of Fluorapatite and Kaolinite in the Presence of Potato Starch, Amylose and Amylopectin.
Figure 6.56 - Degree of Flocculation of Fluorapatite and Kaolinite in the Presence of Tapioca Starch.
Figure 6.57 shows the effect of pH on the flocculation of fluorapatite and kaolinite with 10mg/l of tapioca starch.

The pH dependence of the degree of flocculation closely follows that of the adsorption. Similar results were recently reported by da Luz (1987) for an apatite/starch system. An analysis of the data presented in figures 6.55 to 6.57 provides the following points:

(i) - adsorption of starch on fluorapatite promotes its flocculation;
(ii) - flocculation of kaolinite is small under the conditions tested;
(iii) - starch concentration ranges needed to promote flocculation are similar to those used in the adsorption test programme;
(iv) - amylose (lowest molecular weight) causes less flocculation than the other starches for fluorapatite.

6.5.2 - Graduated Cylinder Tests.

Figure 6.58 shows a comparison between the technique used in the present work (100cm$^3$ graduated cylinders) and a more standard settling test, generally used for thickener design (1000cm$^3$ graduated cylinder). Both settling curves were obtained for fluorapatite pulps containing 3.9% solids
Figure 6.57 - Degree of Flocculation of Fluorapatite and Kaolinite as a Function of pH.
Figure 6.58 - Settling Behaviour of Fluorapatite Suspensions.
by wt. at pH 10 in the presence of 5 mg/l tapioca starch. The two curves present the characteristic linear section for zone settling rates. In both cases, settling rates were calculated as the slope of the two linear sections and their values are also shown in the figure. This comparison supports the validity of the tests performed, using the smaller graduated cylinders.

Figure 6.59 shows a situation similar to that encountered in Fig. 6.55. The settling rates for fluorapatite in the presence of potato starch, amylopectin and amylose are shown as a function of the polymer solution concentration (in mg/l), at pH 10. The experimental curves presented in figs. 6.55 and 6.59 show impressive similarity, although the techniques used were different. Under conditions as those in fig. 6.59, quartz and kaolinite suspensions remained totally dispersed.

Figure 6.60 shows the settling rates of fluorapatite in the presence of tapioca and corn starches. It also depicts the effects of aging (in the case of tapioca starch) and shearing (in the case of corn starch). Both corn and tapioca starch additions promoted similarly shaped settling responses. Maximum settling rates were obtained at 15mg/l in both cases. High level additions of the polymer, however, decreased the settling rates extensively. The aged tapioca starch solution and the sheared corn starch solution displayed reduced flocculating activities, as expected.

The phenomena shown in figures 6.59 and 6.60 deserve
Figure 6.59 - Settling Rate of Fluorapatite Suspensions in the Presence of Potato Starch, Amylose and Amylopectin.
Figure 6.60 - Settling Rate of Fluorapatite Suspensions in the Presence of Corn and Tapioca Starches.
close attention. During the adsorption testwork, the release of Ca upon starch adsorption was also investigated. The same supernatant samples from the adsorption tests, used for Ca determinations, were also submitted to tranmittance measurements. Transmittance values provided a rough indication of the state of dispersion/aggregation.

According to tranmittance measurements(*), the best flocculation was achieved at an initial potato starch concentration of 17.5mg/l. This corresponded to the lowest Ca level measured in solution (24ppm). The same procedure applied to tapioca starch demonstrated that the best flocculation was again reached at an initial concentration very close to the minimum Ca level (20mg/l with minimum Ca of 13ppm at 25mg/l).

Assuming that the molecular weight of potato starch is of the same order as that of potato amylopectin (10 million daltons), and that the area occupied by one starch molecule on apatite is approx. $1.6 \times 10^6 \text{Å}^2$ (Steenberg 1982), the fraction of the mineral surface covered by potato starch at the flocculation maximum is estimated to be 0.391. Making similar assumptions for tapioca starch, the fraction is then 0.577.

A different value for the unit area of starch is given by Hanna (1973) at $6 \times 10^4 \text{Å}^2$ per molecule. If this

(* tranmittance measurements should be more sensitive to the overall size distribution of the flocs whereas settling rates are directly affected by the average floc size.
value is used in the above calculations, ridiculously small surface coverages are encountered, viz. 0.016 for potato starch and 0.022 for tapioca starch. These latter results can not be considered realistic. In fact, if saturation adsorption is assumed for the plateau region of the adsorption isotherms of these two starches, the calculated areas per starch molecule resemble closely that obtained by Steenberg (1982). For instance, in the case of potato starch, at a saturation adsorption of approx. 0.84 mg/m², the calculated unit area is $1.97 \times 10^6 \text{Å}^2$ per molecule (as compared to $1.6 \times 10^6 \text{Å}^2$ found by Steenberg).

According to many researchers (see Steenberg, 1982 for a critical review of the literature on this subject), the flocculation maximum should occur when the fraction of the surface covered is approx. 0.5. This value compares well with the results obtained above.

More extensive surface coverage by polymers might lead to steric (or electrosteric) stabilization (Napper, 1983). In the cases of corn and tapioca starches (Fig. 6.60) there was a considerable reduction in the settling rate at large starch additions. This reduction was also associated with an increase in the visually assessed turbidity of the supernatants. Similarly shaped settling rate/polymer dosage curves can be found in the literature (La Mer and Smellie, 1956 and Somasundaran et al., 1984).
6.5.3 - Effect of Ca Ions.

As indicated in the pioneering work of La Mer and Smellie (1956) the presence of cations, such as Ca(II), is necessary to produce complete flocculation of phosphate slimes. Their interpretation was centred on the formation of insoluble phosphate salts (such as Ca phosphate) during the adsorption of a phosphorus rich modified potato starch (FLOCGEL). In their own words, "the effectiveness of potato starch ... was attributed to the cross-linking made possible by cations (such as Ca\textsuperscript{++}) producing insoluble phosphates with the production of a three-dimensional network and hence large flocs".

Inorganic electrolytes can act as coagulants, promoting aggregation by reducing the electrostatic repulsion (according to the DLVO treatment). Calcium chloride indeed decreases the absolute negative value of fluorapatite's surface charge at pH 10. Therefore, it should not be a surprise to observe an increase in the settling rate of fluorapatite in the presence of Ca ions. Figure 6.61 shows exactly this contribution. Settling rates were almost doubled in the presence of $1 \times 10^{-3}\text{CaCl}_2$.

If the assessment made earlier that surface coverage plays a major role in polymer flocculation, the observed increase in settling rate is probably more related to an increase in the average floc (aggregate) size than to increased adsorption. The curves presented in Fig. 6.61 in
Figure 6.61 - Effect of Ca Ionic Species on the Settling of Fluorapatite Suspensions in the Presence of Tapioca Starch.
the absence and presence of CaCl₂ also show the same overall shape with diminished settling rates at high polymer additions. This similar behaviour in both systems corroborates the proposed explanation. Although adsorption of tapioca starch is known to increase significantly in the presence of Ca ions, it does not lead to a different settling behaviour. The shift towards higher settling rates with similarly shaped settling curves, shows clearly that maximum flocculation is a function of the surface coverage.

In summary, the major aspects regarding the flocculation of apatite with starches are as follows:

(i) - the flocculation caused by amylose is smaller, for the concentration range investigated, than that imparted to fluorapatite by all other starch samples tested;

(ii) - flocculation is dependent on pH, presence of Ca ions and surface coverage of the polymer:

(iii) - Ca ionic species probably participate in the flocculation process by providing anchoring sites for bridging of starch molecules and also by increasing the overall ionic strength of the medium.

(iv) - maximum flocculation is found at surface coverage ratios smaller than 0.6.
6.6 - Microflotation Studies: Starch as a Depressant.

6.6.1 - Floatability of Fluorapatite in the Absence of Starch

Hallimond Tube microflotation has been widely used when the flotation behaviour of pure minerals is under investigation. A modified version of the re-designed Hallimond tube of Fuerstenau et al. (1957), was used in all tests reported herein.

This technique is very simple and can give very reproducible results with relative ease. Operational and experimental details are given elsewhere (Fuerstenau et al., 1957 and in the Experimental chapter of this thesis).

It is very important to recognize clearly the limitations of this technique. Hallimond tube tests provide the mineral processing researcher information on a relatively limited basis. It does have advantages over other "micro" static tests such as vacuum flotation and bubble pick-up. However, Hallimond tube microflotation tests give results that represent only a relative measure of the "floatability" of a mineral under certain pre-established and controlled conditions. It is the opinion of this author that indiscriminate use of the term "recovery" in Hallimond tube test results may convey the wrong idea that a mineral can or can not be recovered in a flotation operation under similar conditions to the ones utilized in Hallimond tube tests. The
use of a less compromised term such as "%Floatability" ("or % weight floated") is preferred and should always be accompanied by information regarding the time of the microflotation test run (and other operational details). Sixty seconds has been the most frequently used time span for Hallimond tube tests.

Another aspect of microflotation tests is flotation by mechanical entrainment of particles, caused by a combination of factors such as agitation level, gas flowrate, height of the flotation column in the Hallimond tube, and of course the size range and specific gravity of the mineral particles being tested. In the present work, particles in the size range of -212+150 m were selected. The entrainment characteristics of the tube used are shown in Figure 6.62, for the following operational parameters: air flowrate = 40cm$^3$min$^{-1}$, room temperature (in the range of 19 to 23 degrees C), and approximately 1g of mineral sample. In figure 6.62 the cumulative % flotability of fluorapatite (Monteiro) in distilled water (pH 6) is plotted against time, up to 15 minutes. For these tests the Hallimond tube was cleaned with extreme care (three times) by the nitric acid/ethanol procedure(*). This procedure was normally only used once when changing reagent systems. Since most test runs in the present work lasted 60 seconds, an

(*) This procedure consists of adding concentrated nitric acid to the vessel to be cleaned, followed by dropwise addition of ethanol until a strong oxidation reaction is initiated (the vessel is wetted by the reacting liquid and thoroughly washed with a large volume of d.w.)
Figure 6.62 - Hallimond Tube Entrainment Related Floatability.
entainment related % floatability of approx. 1% was considered small enough and no adjustments in the operational conditions were made.

6.6.1.1 - Sodium Oleate

Figure 6.63 shows Hallimond Tube floatability results for fluorapatite (Monteiro) in the presence of six different Na Oleate concentrations as a function of pH. The pH range from pH 3.5 to pH 11.5 was investigated. The concentration range for Na Oleate was from $1 \times 10^{-5}$ mol/litre to $1 \times 10^{-4}$ mol/litre.

For the lowest concentration tested, a maximum in the % floatability was found at pH 7.5. The same picture was repeated for the two concentration levels above. At $5 \times 10^{-5}$ mol/litre Na Oleate, the maximum was very broad, occupying the pH range from 7.5 to 10.5. For the highest concentration, % floatability was almost pH-independent above pH 7.5 up to pH 11.5 (95% floatability).

Comparing the results in Figure 6.63 with the results found in the literature (see section 4.3.2), the pH range for maximum floatability at the lowest collector concentration was in good agreement with most of the published data for the apatite/oleate system. Some researchers (e.g. Smani et al., 1973), found two maxima in the microfloation tests on apatites with Na Oleate. One of the two maxima was situated always at pH < 4.5, and was
Figure 6.63 - Microflotation of Fluorapatite in the Presence of Na Oleate as a Function of pH.
interpreted as resulting from the adsorption of oleic acid molecules. On the other hand, the stronger flotation response at neutral pH conditions is associated with the formation of calcium oleate upon adsorption of oleate ions. This latter mechanism is still the most accepted (Leja and Johnston, 1978; Johnston, 1969; Somasundaran et al., 1985). Very recently, Moudgil and co-workers (1986) presented a detailed account of the adsorption mechanism of oleate on apatite, including the identification of rate limiting steps. Another aspect that should be pointed out is the importance of sample history (origin and preparation), especially in the case of minerals such as apatite. This aspect can be responsible for significant differences in microflotation behaviour (see examples in Silva et al., 1985). An alternative explanation for the flotation behaviour of minerals submitted to weak electrolyte collectors, such as Na Oleate has been recently advanced by Castro et al., (1986), Vurdela and Laskowski (1987), and Laskowski (1987). These researchers propose that the low pH floatability behaviour displayed by many minerals in the presence of Na Oleate and other similar collectors, and always associated with physical adsorption of neutral oleic acid molecular species, is better explained by the precipitation of collidal collector species on the surfaces of the minerals in question (also see next section for details).
6.6.1.2 - Dodecylamine Hydrochloride

Cationic collectors used in phosphate flotation usually play the role of gangue collectors. They have the potential for use as apatite collectors in some instances. In both cases, a more complete understanding of their action in apatite systems is important.

Figures 6.64 and 6.64a (for a more detailed look at the pH range of interest) show the microflotation results obtained at six different concentrations of dodecylamine hydrochloride (DDAHC1), again as a function of pH. Flotation pH is a very important variable. It acts on flotation pulps in many ways, such as:

(i) - controlling surface charge of minerals;
(ii) - controlling the hydrolysis of reagents and ubiquitous ions; and
(iii) - controlling the adsorption of reagents onto mineral surfaces, thus controlling selectivity.

The effect of pH on the microflotation response of fluorapatite with DDAHCl was, in many aspects, different than that shown by Na Oleate. The ranges of concentration and pH covered in both cases were similar. At the lowest DDAHCl concentration (1 x 10^{-5} mol/l) tested, the floatability was
Figure 6.64 - Microflotation of Fluorapatite in the Presence of DDAHCl as a Function of pH.
Figure 6.64a - Detail of the Microflotation Response of Fluorapatite in the Presence of DDAHCl as a Function of pH.
very small and practically independent of pH. As the concentration was increased, floatability also increased. At $5 \times 10^{-5}\text{mol/litre}$ collector concentration floatabilities of 70% and higher were achieved in the pH range from 5.5 to 9.5. At the highest concentration, a 90% floatability plateau was present from pH 4.5 to pH 10. Above pH 10, the curves for the three highest concentrations levels displayed an unusual pattern, showing in a very narrow pH range both a maximum and a minimum. Because of peculiarities in microflotation responses above pH 9, the discussion will emphasize the pH range from 9 to 11.5.

One of the most accepted hypotheses concerning adsorption of anionic and cationic collectors (non-thio ionizable surfactants) is the hemi-micelle/electrostatic interaction "theory", advanced by Gaudin and Fuerstenau (1955). Since then, an enormous amount of research work has been carried out in many different flotation systems. The hypothesis assumes that the interaction between collector and mineral surface occurs primarily via an electrostatic attraction between the ionic polar head of a surfactant ion and oppositely charged sites on the mineral surface (ions of the collector would act as counter-ions in the double layer). Upon adsorption, a second mechanism takes place, involving interactions among the hydrocarbon chains of adsorbed collector species. This interaction would lead to the formation of aggregates called hemi-micelles at the solid/liquid interface. For many mineral flotation systems
this picture fits well the available experimental data (adsorption, contact angle, microelectrophoresis and microflotation tests). One of the best arguments in favour of the hemi-micelle hypothesis is the very good correlation among the experimental data (Fuerstenau, and Urbina, 1987). Later, Finch and Smith (1973) and Somasundaran (1976) advanced a new hypothesis, incorporating further experimental and theoretical information on the increased surface activity for amines in the pH range from 8 to 11. In this pH range, ion-molecular complexes were supposed to form. These complexes would then explain rapid flotation for many primary amine/mineral systems under slightly alkaline conditions.

Primary amines are weak electrolytes. The pKa for dodecylamine is 10.63, its solubility limit is 2 x 10^-5 mol/litre and its CMC is 1.3 x 10^-2 mol/litre (Somasundaran, 1976). Below the solubility limit no association of the aqueous species is expected, regardless of the pH. However in the concentration range between the solubility limit and the CMC, depending upon the pH, different pre-micellar associations can occur for dodecylamine solutions.

In recent investigations by Laskowski and co-workers (Castro et al., 1986; Vurdela and Laskowski, 1987, Laskowski, 1987) these associative interactions among ionizable and molecular species resulting from hydrolysis of dodecylamine and other surfactants were extensively investigated. Some of their major findings were as follows:
Figure 6.65 - Microflotation of Apatite from Itataia in the Presence of DDAHCl as a Function of pH.
(i) - dodecylamine colloidal precipitates exhibited an iep at approx. pH 11

(ii) - microflotation of quartz in the presence of DDAHCl at different concentrations above the solubility limit displayed a depression (which was concentration dependent) in the pH range from 10 to 12. As pH was increased floatability increased again to decrease eventually to almost nil at very high pH values.

Smith (1987) also presented similar microflotation results for quartz in the presence of dodecylamine HCl. His results showed depression in the pH range from 9 to 11, followed by a secondary maximum at approx. pH 12.

Although these results are similar to the results shown in Figure 6.64, the pH range where both depression and the secondary floatability maximum are observed is different for the fluorapatite system.

To confirm that the results obtained were not caused by a sample related artifact, another apatite sample was submitted to microflotation with DDAHCl (5 x10^{-5} mol/litre). The results, shown in Figure 6.65, confirmed the previous findings.

The apatite/amine system presents an extra complicating factor: the presence of phosphate ionic species.
Soto and Iwasaki (1984 and 1986) proposed that chemisorption takes place in primary amine/apatite systems. Their claim was supported by thermochemical measurements of heats of adsorption and solubility testwork. The heats of adsorption for primary amines on francolite surfaces at low adsorption densities were found to be exothermic and very close to the heats of reaction of amine with phosphate ions.

One possible explanation for the observed depression followed by a secondary floatability peak at a different pH range from that reported in the literature would call for a combination of the newest interpretation given by Laskowski and co-workers with the very plausible chemisorption mechanism of Soto and Iwasaki. Both the depression and the secondary floatability peak have been interpreted as being caused by the precipitation and redispersion of the colloidal collector species. The pH range for such reactions can, however, be altered. In the amine/apatite system parallel reactions involving chemical bonding between ammonium and phosphate ions are taking place. At $5 \times 10^{-5}$ mol/litre of DDAHCl the onset of depression in the flotation of fluorapatite occurs at pH 9.3, whereas at the same concentration the onset of depression for quartz starts at pH 10 (Laskowski, 1987). Maximum depression for fluorapatite was found at pH 10.4 while for quartz it occurred at pH 12.0. The secondary floatability peak occurred at pH 10.8 for fluorapatite and at pH 12.5 for quartz. It seems that the same phenomenon is occurring in both cases,
however at different pH values. This difference in pH could be caused by amine chemisorption. In the presence of phosphate sites the relative concentration of ionic surfactant species would decrease more rapidly at a lower pH, hence the whole process was shifted towards a lower pH range.

6.6.2 - Action of Starches.

As already mentioned, starches are employed to perform a variety of different tasks in the beneficiation of phosphate ores. One of the most common functions is as a depressant for carbonates (calcite and dolomite) and ferriferous (hematite, limonite, goethite, iron silicates) gangue minerals.

In this section, the depressant action of starches on fluorapatite was tested for both anionic and cationic collector systems.

Figure 6.66 depicts the effect of amylose, amylopectin and potato starch on the floatability of fluorapatite in the presence of $5 \times 10^{-5}$ mol/litre Na Oleate at pH 10.5. Of the two starch fractions, amylopectin caused stronger depression than amylose. This can be partially attributed to the more extensive adsorption of amylopectin on fluorapatite. Both potato starch and amylopectin showed similar behaviour. The onset of constant depression occurred at 10mg/l for amylose and at 5mg/l for amylopectin and potato starch. Experimental conditions for these tests included a
Figure 6.66 - Effect of Potato Starch, Amylose and Amylopectin on the Microflotation of Fluorapatite with Na Oleate.
five-minute conditioning for starches and a one-minute for collectors. Under such conditions (which were chosen after some preliminary reproducibility tests) starch adsorption might not have reached equilibrium even though the available surface area for the much coarser fluorapatite particles used in the microflotation tests, was much smaller than in the adsorption tests. Hence, a direct comparison between the concentration for maximum depression obtained and that for saturation adsorption should not be attempted.

Figure 6.67 shows similar results for tapioca starch. Again strong depression occurred at very low starch additions. The lowest % floatability is the same as was achieved before for potato starch and amylopectin.

At pH 7.5 the depression caused by all starches tested was smaller than at pH 10.5. These results are presented in table 6.XVI. The observed pH dependence of the depressant action of starches is in line with the adsorption results. This smaller depressant effect can also reflect the larger affinity of Na Oleate for fluorapatite surfaces at pH 7.5 as compared to pH 10.5.

As previously shown, both amylose and amylopectin interact with Na Oleate. Ultraviolet-visible spectra of amylose and amylopectin in the presence of iodine and Na Oleate showed increased interaction at more basic pH conditions. These findings also support the stronger depressant action at high pH values.
Figure 6.67 - Effect of Tapioca Starch on the Microflotation of Fluorapatite with Na Oleate.
With an increase in the concentration of Na Oleate, the depression is reduced, as shown in Figure 6.68 for potato starch. If one compares the results in terms of collector/depressant ratios, the effectiveness of the depression caused at the higher collector concentration is many times lower. This situation probably indicates that starches act as depressants not by eliminating (or decreasing) collector adsorption. In fact under certain conditions starch enhances collector adsorption (Khosla, 1983). This researcher proposes three distinct possibilities to explain the adsorption of starch in the presence of surfactants:

(i) - decreased collector adsorption through the classical competition between adsorbing species;
(ii) - enhanced collector adsorption by accommodating collector within the amylose helices;
(iii) - induced co-adsorption through binary interactions.

Strong depression occurs at low collector concentration but the much smaller depressant action as the collector concentration is increased seems to favour (ii) and/or (iii) above. Table 6.XVII presents the results for other starches at a higher collector concentration (1 x 10^{-4} mol/litre). These results support the idea that
Figure 6.68 - Depression of Fluorapatite by Potato Starch at a Higher Na Oleate Level.
starches depress the floatability of fluorapatite not by suppressing the adsorption of the collectors.

Figure 6.69 shows the effect of potato starch, amylopectin and amylose on the floatability of fluorapatite with dodecylamine hydrochloride \(5 \times 10^{-5}\) mol/litre, pH 9.2). These results are similar to those presented for Na Oleate (Fig. 6.66). However, the depression promoted by amylose is smaller for the DDAHCl case. This might reflect the smaller ability of cationic surfactants to react with amylose by being entrapped inside the helices. Figure 6.70 shows the effect of tapioca and corn starches, which again is similar to that caused either by potato starch or potato amylopectin.

The effect of increasing the collector concentration is presented in table 6.XVIII for tapioca starch. The results showed that at increasing DDAHCl concentrations, the depressant action was diminished and eventually suppressed completely.

The results obtained for the DDAHCl system give further support to the idea that starch does not impede collector adsorption.

In summary, the roles of amylose and amylopectin in starch depressant action are probably different. Amylose reacted more readily with surfactants, but the larger and more extensively adsorbed amylopectin macromolecule dominated the depression. Most of the starches used in mineral processing are amylopectin-rich (potato, corn and tapioca).
TABLE 6.XVI  Effect of pH on the Depressant Action of Starches  
(Na Oleate - $5 \times 10^{-5}$ mol/litre; Starch - 10.5mg/l)

<table>
<thead>
<tr>
<th>Starch</th>
<th>% Floatability</th>
<th>pH 7.5</th>
<th>pH 10.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potato Amylose</td>
<td>61</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>Potato Amylopectin</td>
<td>45</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>Potato Starch</td>
<td>53</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>Tapioca Starch</td>
<td>47</td>
<td>14</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 6.XVII - Effect of Collector Concentration on the Depression Caused by Starch (starch = 21 mg/l)

<table>
<thead>
<tr>
<th>Starch</th>
<th>% Floatability</th>
<th>Na Oleate $5 \times 10^{-5}$mol/l</th>
<th>$1\times 10^{-4}$mol/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potato Starch</td>
<td>10</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>Potato Amylose</td>
<td>18</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>Potato Amylopectin</td>
<td>14</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>Tapioca Starch</td>
<td>10</td>
<td>52</td>
<td></td>
</tr>
</tbody>
</table>

pH = 10.5
Figure 6.69 - Effect of Potato Starch, Amylose and Amylopectin on the Microflotation of Fluorapatite with DDAHCl.
Figure 6.70 - Effect of Tapioca and Corn Starches on the Microflotation of Fluorapatite with DDAHCl.
TABLE 6.XVIII  Effect of the Collector Concentration on the
Depression Action of Tapioca Starch
(Tapioca Starch-42mg/l; pH 9.2)

<table>
<thead>
<tr>
<th>DDAHCl (mol/litre)</th>
<th>% Floatability</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5 \times 10^{-5}$</td>
<td>8</td>
</tr>
<tr>
<td>$1 \times 10^{-4}$</td>
<td>30</td>
</tr>
<tr>
<td>$3 \times 10^{-4}$</td>
<td>55</td>
</tr>
<tr>
<td>$5 \times 10^{-4}$</td>
<td>100</td>
</tr>
</tbody>
</table>
The suppression of hydrophobicity imparted by starches is likely due to the ability of adsorbed polymer molecules to interact with the adsorbing surfactant species in such a manner that the hydrophobic hydrocarbon chains are occluded within the polymer molecules. Increased collector addition leads to the return of hydrophobicity.
7 - GENERAL DISCUSSION

7.1 - The Importance of Starch Solution Preparation

Research performed in this thesis gave evidence of the great importance of the preparation (and storage) of aqueous starch solutions.

This aspect has been the subject of attention by many researchers. In all cases, three major points should be emphasized:

(i) aging of the solutions, independently of the mechanisms responsible for it, affects the results considerably;

(ii) degradation of the polymer solutions (molecular weight decrease) takes place due to either excessive agitation ("shearing") or sonic irradiation;

(iii) cold gelatinization is sufficient to obtain good dissolution of the starch samples used, however heating at 45°C of the water utilized for dilution of the gel obtained by adding NaOH to the initial starch suspension improves the quality of the final solution.
In the case of aging, minute amounts of visible precipitates are a good indication of the process taking place. The solution also becomes more turbid and the turbidity measured by light scattering decreases. The sometimes suggested (and used) storage at low temperature has no technical basis whatsoever. Retrogradation rates increase as the temperature is decreased. Laboratory work using starch aqueous solutions must always be performed with freshly prepared (same day) solutions. This problem is not always detected because most industrial applications of starch in mineral processing occur in plants that run continuously. During long plant shut downs, starch solution storage tanks should be emptied and fresh solutions prepared just before the plant is re-started.

Degradation by physical means is a phenomenon that never should be overlooked. Sheared polymer solutions have their flocculation power diminished. Suitable preparative procedures are an important prerequisite in the use of starch solutions.

Cold (caustic) gelatinization is the preferred method for starch solution preparation in mineral processing applications. One of the reasons is simply that the processing stages are generally performed in alkaline circuits (viz. reverse cationic flotation of iron ores and direct anionic flotation of phosphate ores). In this way, the starch solution also plays (totally or partially) a role
as a pH modifier. In the laboratory, if short preparation times are required (or desired), heating of the dilution water to a temperature below the gelatinization temperature for the starch in question, decreases the time required to obtain reproducible and well prepared solutions.

In summary, the procedure employed in the preparation and storage of starch solutions play a major role in the results obtained. Although this concern has been realized by many researchers, one still can find in the modern literature technical papers describing the use of starch solutions kept in a refrigerator for over a week (Somasundaran, 1968). Another even more basic fact concerning starches is the type of starch used. Some authors seem to consider starch as a well defined chemical compound, with unique properties regardless of its source. This, of course, is not true. Again, the detailed description of the starch(es) employed in any research programme is of paramount importance.

7.2- Selectivity of Adsorption

The adsorption test programme carried out in the present work indicated that starches possess higher affinity for apatite surfaces than for quartz. Although this result can not be considered as unexpected in view of the available literature, the mechanisms responsible for this behaviour deserve more attention. The results also showed that Ca
species increase considerably the adsorption of starch onto mineral surfaces. Even for quartz, on which starch was adsorbed only in very small quantities, the presence of Ca ions increased many times the amount adsorbed.

Assuming first that electrostatic forces are of primary importance, the much larger extent of adsorption of starch on apatite at pH 10 as compared to that on quartz at the same pH should not have occurred. Both minerals displayed negatively charged surfaces at this pH (electrophoretic mobilities of -4 and -3 micron/s per cm/V for quartz and apatite, respectively). If only electrostatic repulsion is considered as the reason for the smaller adsorption on quartz, assuming that both surfaces are equally capable of performing hydrogen bonding, then at least the shapes of the adsorption isotherms would be similar. As demonstrated earlier, they are not similar. The adsorption at low starch residual (equilibrium) concentrations is very high for apatite. Also, the isotherms on quartz do not show a plateau region in the range of concentration tested. The electrical double layer on both surfaces should be populated by cations as counter-ions at pH 10. However, in the case of apatite, Ca$^{2+}$ ions dissolving from the surface should also be situated at the interface. In turn, being much less soluble, counter-ions at the quartz/ water interface should be predominantly H$^+$. 

The affinity between starch and Ca ions was demonstrated by the conductivity test programme. Starch
molecules should possess an extra force driving them to the apatite/water interface. This extra force is necessary to overcome the presence of electrostatic repulsion since starch molecules carry negative charge.

Thus, one of the reasons for the preferential adsorption of starches on apatite as compared to quartz, is probably the presence of Ca ions. This explains partially why, in the presence of Ca ionic species, the amount of adsorption on quartz also increases.

Nevertheless, the adsorption on apatite is also greater than that on quartz in the presence of Ca ionic species because the starch macromolecules attracted to the apatite/water interface have on the surface of this mineral, Ca sites for a more stable anchoring. Therefore the extent of adsorption is much higher in this case.

Another aspect favouring the small relevance of electrostatic forces, is that the adsorption of starches on apatite did not decrease as the pH was increased (i.e. the negative value of the surface charge also increases). The increase in pH should also be accompanied by an increase in the concentration of Ca ions at the interface.

The shape of the Ca release curves upon adsorption of starch on apatite is another important result. At equilibrium concentrations smaller than the concentrations required for the plateauing of the isotherms, there is a considerable decrease in the amount of Ca ions in solution. This phenomenon might be related to the complexation of these
ions by starch macromolecules. One can even speculate on a mechanism of adsorption involving the precipitation of starch/calcium complexes on the surface of apatite. The complexation properties of starches are a well known fact, especially in the food technology literature, as already mentioned.

In summary, the adsorption mechanisms of starch on apatite are dependent on:

(i) - presence of Ca species both at the interface and at the surface;
(ii) - pH;
(iii) - molecular weight of the starch in question.
(iv) - polymer conformation in solution.

In view of results obtained and discussed, the following mechanisms are proposed:

a - the strongest driving force operating is due to the high affinity between Ca ionic species and starch. The reasons for this affinity can be found in the presence of ionic impurities present in the starch macromolecules, most probably those containing carboxylic and phosphate groups;
b - the importance of hydrogen bonding can not be ruled out. Since the polymers are
constructed basically from intramolecular H bonds, these forces will be present also in the overall adsorption forces;

c - the electrostatic component of the adsorption forces should be of minimal significance, especially if this type of force is used to explain the preferential adsorption on apatite.

d - higher adsorption at more alkaline conditions may reflect the presence of more extended macromolecules in such solutions.

7.3 - The Role of Starches in Apatite Flocculation Systems

The most interesting use for starches in apatite systems is as a selective flocculant in selective desliming applications. All of the literature available on this subject presents data on the successful use of starches (modified or non-modified) playing the role of selective flocculant. The systems studied involve generally phosphate ores with predominant siliceous gangue minerals. Another constant in such studies is the use of an alkaline pH for maximum selectivity.

The results obtained in the present work fully support the selective action of starch in the systems described above. The adsorption of these macromolecules on
apatite surfaces is much higher than that obtained on quartz and kaolinite. The pH range for maximum adsorption is also in line with the use of alkaline pH values for the selective flocculation studies. One can then ask the question: Why hasn't selective flocculation (or selective desliming) encountered any industrial application in the treatment of phosphate ore with predominant siliceous gangue? There are many answers to that question. First, there is an economic reason. The implementation of a selective desliming stage in operating systems will have a considerable cost. Second, and more important, selective flocculation as a way to concentrate phosphate ores will not work in most cases. Although there is considerably more adsorption on apatite, the small amount of starch adsorbing on siliceous minerals, associated with the complicating factor of the presence of dissolved ionic species, hinder the achievement of high enrichment ratios in such operations. One can also recall the entrapment of dispersed phase particles within the structure of the flocs formed. All of these problems make the use of selective flocculation, as proposed by many authors as a concentration unit operation for fine phosphate ores, practically impossible, unless new means are devised to separate flocculated and dispersed phases. These new processes would have to minimize the physical entrapment of dispersed particles into the flocs.

The use of selective desliming with starch also acting as a selective flocculant (but without the compromise
of requiring high enrichment ratios) might be one possible solution to increase the overall recovery of phosphate. This route was described in detail by de Araujo et al. (1986), who used successfully corn starch as a selective flocculant for sedimentary phosphate ores. The process, tested only at bench scale, involved the selective desliming of the ores followed by flotation of apatite with an anionic collector. Along the same line, reverse cationic flotation of gangue minerals can also be used after the selective desliming procedure (this second possibility is basically the same process scheme used for iron ores, the sole true application in industrial scale of selective desliming/flotation).

The other possible application of starches in apatite systems is the use of such polymers as "bulk" flocculants, in solid/liquid separation. Although most of the applications of starches as bulk flocculants have ceased since the introduction of synthetic flocculants (polyacrylamides, polyacrylates, etc.), they are still encountered, for example, in the Brazilian iron ore industry. One possible difficulty involves the residual starch, introduced back into the circuit with the reclaimed water. As will be seen in the next section, starches also play the crucial role as depressant agents for the difficult apatite/calcite flotation separation. In such cases, the presence of residual starch in the circuit might affect flotation performance.
One of the most challenging flotation separations is that of selectively floating apatite from calcite and other carbonates. So far, this has been possible on an industrial scale in very few cases, all of them involving well crystallized minerals, from igneous phosphate deposits. In such separations, starches play a very important role - they selectively depress calcite, allowing for the anionic flotation of apatite. Plant practice involves an alkaline circuit (pH between 10 and 10.5) and conventional anionic collectors, such as tall oil. The actual role of starch in this process seems to be of preventing (or diminishing) the adsorption of the collector on calcite surfaces, thus leaving apatite surfaces amenable for the adsorption of collector species.

The results obtained in the present work showed that Ca ionic species influenced remarkably the adsorption behaviour of starches on minerals surfaces. The selective depressant action displayed by starches in apatite/calcite systems is indirect evidence of the very high affinity existing between Ca and starches. In the presence of a surface that has even more Ca sites and Ca ionic species at the water interface, starch prefers the calcite surface in comparison to the apatite surface. There must be an equilibrium condition such that the amount of starch added to the system is sufficient to cover the calcite surfaces,
while not affecting apatite. Plant practice corroborates this hypothesis, since an increase in starch dosage above the ideal level leads to a decrease in grade of the concentrate obtained.

Concerning the modes of action in systems involving starch as a depressant, the experimental work described herein indicates that they are dependent on the pH, collector/starch ratios and starch type. The effect of pH parallels the adsorption results, i.e. maximum depression of apatite microflotation in the presence of Na Oleate occurred at an alkaline pH, close to the pH of maximum starch adsorption. At pH 7.5 all starches depressed apatite to a much smaller extent than at pH 10.5. These results contribute to an hypothesis favouring the complexation of collector species at the interface, more than in bulk solution. The interaction of starches with the collectors in the absence of the mineral also indicated a stronger interaction at alkaline pH values. The first hypothesis that maximum starch adsorption leads to increased depression should not be taken as completely satisfactory. The maximum floatability rate for apatite in the presence of Na Oleate occurs near neutral pH conditions. Thus, the diminished depressant action of starches at this pH can reflect only the condition of the surface, more hydrophobic at pH 7.5 than at pH 10.5, in the presence of Na Oleate. Actually two different mechanisms are probably being superimposed in this case: maximum adsorption of the depressant does occur at an
alkaline pH and it is also at alkaline conditions where the strongest starch/surfactant interaction takes place. Both mechanisms should contribute to the results obtained.

The second aspect, involving the relative amounts of starch and collector species present in the system, indicate that an increase in the concentration of the collector for a fixed amount of starch, leads to the re-establishing of flotation. In such a case, the most probable mechanism in operation would call for the adsorption of collector species on a starch coated surface. This means that starch does not impede the adsorption of collector species. Even more, the starch/collector complexes formed either in solution or upon adsorption are themselves dependent on the relative amounts of each constituent. It is a reasonable assumption that part of the collector reacted with the starch macromolecules stays inside the helical portions, especially of amylose. These portions of the collector can then be considered as inactive in terms of making the surface hydrophobic. Upon increasing the amount of collector, it might still interact with starch species, but now, the collector hydrophobic chains will be available for the hydrophobization of the surface, hence flotability is resumed.

In summary, starch can act as a depressant in both anionic and cationic flotation of apatite. The depressant action is a combination (summation) of effects, involving the adsorption of the depressant onto the mineral surfaces and the interaction occurring between starch and surfactant
species. The preferential adsorption of starches onto a specific mineral can be considered as more relevant to the final depressant action than the interaction between starch and collector species. This idea is supported by the fact that starch can be and is used as a selective depressant in the flotation of apatite from calcite.
8 - CONCLUSIONS

1 - Starch samples used in the present work were extensively characterized in terms of molecular weight, solution preparation and storage, reaction with surfactants, reaction with Ca ions and presence of impurities. The most relevant findings were:

a) - As expected, amylose has a much smaller molecular weight than amylopectin.

b) - Aqueous solutions of starch can become degraded by: storing, both below and above room temperature; shearing and when subjecting to sonic baths. The degradation of these solutions can be followed by light scattering measurements.

c) - Both starch fractions were found to react with Na Oleate and dodecylamine hydrochloride, as indicated by UV-visible spectroscopy in the presence of iodine. Reaction with surfactants by amylose was explained in terms of the entrapment of surfactant species inside the helices of the polysaccharide.

d) - Starch fractions and starch samples were found to react with Ca ionic species. This reaction was followed by the depression of
solution electrical conductivity upon mixing Ca and starch solutions. Alkaline solutions favoured a stronger reaction.

e) - Impurities in starch samples were probed by infrared spectroscopy and electrophoresis. Both techniques indicate that all samples used contained some impurities such as proteins and fatty acids.

2 - Apatite samples of different origins were characterized mainly by infrared spectroscopy. Quartz and kaolinite were also characterized by the same technique.

3 - Dispersion and electrophoresis studies on mineral samples indicated the following important findings:

   a) - Fluorapatite, quartz and kaolinite displayed their highest suspension stability under alkaline pH conditions. Commonly used dispersants enhanced the stability of mineral suspensions under most conditions tested.

   b) - Presence of ubiquitous ionic species such as Al, Ca and Mg promoted significant changes in the electrophoretic mobility/pH curves for fluorapatite and quartz.
Adsorption of starches onto fluorapatite and quartz surfaces showed the following relevant aspects:

a) - Adsorption was influenced by molecular weight. Amylopectin adsorption in a mg per unit area basis is greater than amylose adsorption on fluorapatite.

b) - Adsorption onto fluorapatite surfaces (as well as on hydroxyapatite) is many times larger than the adsorption on quartz (as well as on silica). The higher affinity of starches for apatite surfaces was explained in terms of Ca/starch reactions, taking place most probably at the interface.

c) - Presence of externally added Ca species increased the adsorption of starches onto both apatite and quartz.

d) - Moderately alkaline pH conditions enhanced starch adsorption on apatite.

Flocculation of fluorapatite, quartz and kaolinite by different starches gave the following major findings:

a) - Amylose has the smallest ability to flocculate apatite suspensions as compared to all other starches tested.
b) - As indicated by the highly preferential adsorption of starches on apatite as compared to quartz, flocculation of apatite suspensions was very effective in the presence of these polymers. In turn, kaolinite and quartz suspensions were not affected by starches under the conditions tested.

c) - Flocculation of apatite by starches was enhanced in the presence of Ca ionic species.

d) - Maximum flocculation parallels adsorption in terms of its pH relationship.

e) - Maximum flocculation occurred under conditions where the surface coverage of apatite by starches was less than 60%.

6 - Flotation of fluorapatite by both anionic and cationic collectors was depressed in the presence of starches. Amylose depression was smaller than the depression caused by amylopectin and other starches. Depression by starches was a function of pH and the relative amount of starch and collector. High pH values favoured depression while increased collector additions diminished (and eventually eliminated) the depressant action of starches. This latter finding supports the idea that starch-related depression is
not caused by impeding collector adsorption but rather by reacting with collector species in such a way that it no longer makes the surfaces hydrophobic.
9 - SUGGESTIONS FOR FURTHER WORK.

Many of the findings in the present thesis warrant further research. Some suggestions are:

1 - Investigate the effects of other ionic species, commonly occurring in phosphate ore pulps, such as Mg, Fe (ferric mainly), Ba, fluoride, phosphate and sulphate, on the adsorption characteristics of starches onto apatite surfaces.

2 - Investigate grafting and chemically modifying starch polymers to make their adsorption even more selective.

3 - Design ways to investigate adsorption of starches onto mineral surfaces, when two (or more) minerals are present at the same time in a pulp. Studies of this type would clearly assist the understanding of selective flocculation and selective depression processes. Sensible carbon analysis techniques could provide the means of measuring directly adsorbed amounts on the minerals.

4 - Thoroughly investigate the mechanisms involved in the cationic flotation of phosphate minerals.
5 - Verify the effects of starch build up in recirculated (recycled) water in plant operations.

6 - Seek an even better understanding of the roles played by each starch fraction in both flocculation and depression.

7 - Investigate the use of small amounts of organic solvents in the preparation of starch solutions. Some organic substances can decrease retrogradation rates and might even facilitate the gelatinization process.
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APPENDIX I - FURTHER CHARACTERIZATION OF MINERAL SAMPLES

1 - APATITE FROM ITATAIA (CEARA STATE, BRAZIL)

This sample was obtained from NUCLEBRAS (Belo Horizonte, Brazil). It is present in a non-typical phosphate deposit, situated in the northeast portion of Brazil. It was received in a purified form, sized between -212+105 micron. It was used for the infrared spectroscopy testwork and in one set of microflotation tests.

When submitted to microprobe analysis (JEOL JXA-3A), elemental mapping of a few grains showed the presence of Fe impurities, evenly distributed over the surface of each grain; probably present as a substitution in the apatite lattice. Silicon was also detected but no definitive information concerning its distribution could be obtained.

Wet chemical analysis (UBC-MMPE laboratories) provided the following results: $P_2O_5=36.7\%$; $CaO=56.18\%$; $Fe(t)=3.573\%$; $Al_2O_3=0.265\%$; $SiO_2=6.15\%$ and $MnO_2=0.063\%$.

2 - APATITE FROM ONTARIO (CANADA)

This sample was previously used in Johnston's UBC (MMMPE) M.A.Sc. thesis (1969). It consisted of massive blue coloured hand picked pieces. It was used only for the infrared spectroscopy testwork. Wet chemical analysis (UBC MMPE laboratories) indicated: $P_2O_5=36.20\%$ and $CaO=52.5\%$.

3 - TRIBASIC CALCIUM PHOSPHATE (FISHER SCIENTIFIC C-127)

This A.C.S. reagent has been used in the literature as representative of hydroxyapatite. It was used for the infrared spectroscopy testwork and for the preliminary adsorption programme. This later use was due to its high specific surface area (approx. 16 sq m/g), which made it possible to make the adsorption as probed by the iodine colour reaction more clearly visible.

4 - Min-U-Sil 5 (SILICA)

This high purity crystalline silica sample was also used in the preliminary adsorption test programme in lieu of quartz for the same reasons as synthetic hydroxyapatite was used. Its analyses and specifications given by the supplier are: $SiO_2=99.7\%; Fe_2O_3=0.023\%$, $L_I(650 \text{ degrees } C)=0.145\%$; $Al_2O_3=0.101\%$; $TiO_2=0.019\%$, specific gravity=2.65; specific surface area=20.6 sq m/g; average particle size=1.9 micron; non-porous.
This clay sample has the following specifications and chemical composition given by its supplier: SiO$_2$ = 45.63%; Al$_2$O$_3$ = 38.51%; Fe$_2$O$_3$ = 0.44%; TiO$_2$ = 1.43%; CaO = 0.24%; MgO = 0.14%; L.I. (at 1000 degrees C) = 31.51%; average particle size = 1.1 micron. This sample was characterized by surface area measurement (BET) and infrared spectroscopy as already described.
The infrared spectra (KBr pellets) of the two collectors used in the present thesis are shown in figure II.1. The main infrared bands are marked on the spectra. Table II.A presents the assignments of the various absorption bands observed. Both sample were found to be free of any major contaminants. All peaks recorded could be assigned accordingly to those found in the literature.

TABLE II.A - Assignments of Infrared Bands of Collectors (Spectra shown in fig. II.1)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Peak Wavenumber (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>SODIUM OLEATE</td>
<td>2925 and 2852</td>
<td>asynd and sym. C-H deformation</td>
</tr>
<tr>
<td></td>
<td>1562</td>
<td>asynd. COO(^{-})vib.</td>
</tr>
<tr>
<td></td>
<td>1454 and 1426</td>
<td>sym. COO(^{-})vib. superimposed to C-H vib.</td>
</tr>
<tr>
<td></td>
<td>1350-1180</td>
<td>COO(^{-})disturbed vib. (wagging, twisting, etc)</td>
</tr>
<tr>
<td></td>
<td>926</td>
<td>out of plane OH angular def.</td>
</tr>
<tr>
<td></td>
<td>723</td>
<td>CH(_2) rocking vib.</td>
</tr>
<tr>
<td></td>
<td>696</td>
<td>=CH out of plane bending/cis form</td>
</tr>
<tr>
<td>DODECYLAMINE HCl</td>
<td>2917 and 2849</td>
<td>asynd. and sym. C-H deformation superimposed to the sym. axial deformation of NH(_3)</td>
</tr>
<tr>
<td></td>
<td>2029 and 2010</td>
<td>N-H(^{+})overtone def. in NH(_3) (very characteristic for primary)</td>
</tr>
</tbody>
</table>
TABLE II.A - Continued

<table>
<thead>
<tr>
<th>Compound</th>
<th>Peak Wavenumber (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>amine salts)</td>
</tr>
<tr>
<td>1627</td>
<td></td>
<td>asym. def. of NH$_3$</td>
</tr>
<tr>
<td>1587</td>
<td></td>
<td>sym. def. of NH$_3$</td>
</tr>
<tr>
<td>1475 and 1462</td>
<td></td>
<td>CH$_2$ asym. bending</td>
</tr>
<tr>
<td>1402</td>
<td></td>
<td>CH$_3$ asym. def.</td>
</tr>
<tr>
<td>1372</td>
<td></td>
<td>C-H sym. def.</td>
</tr>
<tr>
<td>1162-946</td>
<td></td>
<td>C-N stretching vibration</td>
</tr>
<tr>
<td>762</td>
<td></td>
<td>N-H$^+$ out of plane deformation</td>
</tr>
</tbody>
</table>

Notation: asym. = asymmetric; sym. = symmetric; def. = deformation; vib. = vibration

References: Silverstein et al. (1979), Socrates (1980) and Brandão (1982).
Figure II.1 - Infrared Spectra of: (1) Na Oleate and (2) Dodecylamine Hydrochloride.
APPENDIX III - CALIBRATION CURVES FOR STARCH ANALYSIS
AND STARCH SOLUTION PREPARATION

1 - GENERAL

The development of colour due to the interaction of iodine with starches is well documented. For the adsorption testwork involving starches, the analysis of filtrates (i.e. equilibrium concentrations after adsorption) was performed using the colour development of starch solutions reacted with KI/Iodine. A Spectronic 21 U.V./VIS. spectrophotometer was used, equipped with cylindrical, optically clear, glass cells with a constant light path of 10mm. The wavelength was selected individually for each sample, so a maximum absorbance was obtained. The colour developed by the reaction between starch and iodine is stable for many hours, but the intensity is pH dependent. Therefore the measurements were made after the filtrates from the adsorption tests were brought to a previously fixed pH value. In general terms, the intensity of the colour (measured absorbance) increased as the pH decreased.

2 - PRELIMINARY TESTWORK

The standard KI/iodine solution, prepared in a batch of 4 litres of distilled water, contained 0.241 mol/litre KI and 0.005mol/litre Iodine (160g of KI and 2.538g of Iodine in 4 litres). For each test, 0.4ml of the KI/iodine solution was added to the starch solution by using a microburette (maximum capacity of 2ml). The starch test solution had a volume of either 25 or 50ml, as measured by a 50ml graduate cylinder.

The first tests involved the analysis of a freshly prepared potato starch solution, diluted to concentrations varying from 4 to 100mg/litre. The first test solution containing 30mg/litre was scanned through the wavelength range from 550 to 660nm. The maximum absorbance was observed at 586nm and all other test solutions were then analysed at this wavelength and also at 566nm, corresponding to the beginning of the absorbance peak. The pH of all solutions was 6.0. Starch solutions were diluted to 25ml test samples. A blank was prepared by adding 0.4ml of KI/iodine to 25ml of distilled water. The zero absorbance was pre-established as the value obtained with distilled water only. Later in this test programme, the zero absorbance was set with a blank containing 0.4ml of KI/iodine solution. Preliminary results are shown in table III.A and figure III.1. Inclusion of the 100mg/l result at this point was considered, but there was a drop in linear regression correlation coefficient, as shown next:
a) at 566nm
   including 7 data points  \( r = 0.9991 \)
   including all points  \( r = 0.9981 \)

b) at 586nm
   7 data points  \( r = 0.9997 \)
   all points  \( r = 0.9988 \)

<table>
<thead>
<tr>
<th>Concentration (mg/l)</th>
<th>Absorbance at 566nm</th>
<th>Absorbance at 586nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.000</td>
<td>0.070</td>
</tr>
<tr>
<td>4</td>
<td>0.056</td>
<td>0.119</td>
</tr>
<tr>
<td>10</td>
<td>0.108</td>
<td>0.168</td>
</tr>
<tr>
<td>16</td>
<td>0.168</td>
<td>0.229</td>
</tr>
<tr>
<td>20</td>
<td>0.208</td>
<td>0.268</td>
</tr>
<tr>
<td>30</td>
<td>0.297</td>
<td>0.362</td>
</tr>
<tr>
<td>40</td>
<td>0.393</td>
<td>0.456</td>
</tr>
<tr>
<td>100</td>
<td>0.886</td>
<td>0.939</td>
</tr>
</tbody>
</table>

To confirm further the results shown in figure III.1, another set of samples was analysed at 586nm only. The new data are plotted in figure III.2 together with the points from figure III.1. Linearity was obtained up to 100mg/l of potato starch. The points at 150 and 180mg/l show a drop in linearity for concentrations above 100mg/l.

Also shown in figure III.2 is the new best straight line and its corresponding equation and correlation coefficient. Note that the point at 100mg/l can now be safely included in the best line, since a regression analysis now indicates an increase in the correlation coefficient, if the point at 100mg/l is included, as follows:

a) 14 data points up to 90mg/l  \( r = 0.9900 \)

3 - ROUTINE ANALYSIS

Having established that the technique can be used for the analysis of starch solutions up to 100mg/l (except
Figure III.1 - Initial Calibration for Potato Starch.
Figure III.2 - Final Calibration for Potato Starch.

The graph shows the relationship between concentration (mg/litre) and absorbance (586nm) for Potato Starch. The equation of the line is: $A = 0.0088C + 0.0878$, where $A$ is absorbance and $C$ is concentration (mg/litre). The pH is 7.
for potato amylose), a series of calibration curves for the different starch samples used was obtained.

The first difference in this new series of tests was that blanks for zero absorbance consisted of KI/iodine solutions. The instrument was externally adjusted to read zero absorbance at the desired wavelength. A second difference was that a very careful control of pH was observed. The linear regression equations obtained for all starch samples used were as follows (notation =>

Abs = absorbance, CS = concentration of starch in mg/litre, r = linear regression correlation coefficient):

**Potato Starch (at 586 nm)**

Abs = 0.0024(CS) + 0.0071  \( r = 0.999 \)

**Tapioca Starch (at 586 nm)**

Abs = 0.0060(CS) + 0.0255  \( r = 0.998 \)

**Potato Amylopectin (at 556 nm, 1 ml KI/iodine)**

Abs = 0.0048(CS) - 0.0057  \( r = 0.997 \)

**Potato Amylose (at 600 nm up to 30 mg/litre)**

Abs = 0.0227(CS) + 0.0029  \( r = 0.996 \)

More sophisticated statistical analysis of the data indicated that in all cases the partitioning of the total variation was such that a very significant variation was accounted for by the linear models and an insignificant amount of variation was due to the lack of fit. For example, in the case where the lowest correlation coefficient was obtained (potato amylose), the analysis of variances showed a sum of squares of 0.36449 for the model and 0.0029076 for the error, giving an F-ratio of 626.793.

During the test runs involving Ca ions, a new calibration curve was obtained for both potato amylopectin and tapioca starch in the presence of these ions. In the first case the best straight line was coincident with that already mentioned. For tapioca starch however, the following calibration was used:

**Tapioca Starch (at 586 nm and 0.001 mol/litre Ca chloride)**

Abs = 0.0062(CS) + 0.0204  \( r = 0.996 \)
Starch solutions were prepared daily by gelatinization with a strong NaOH solution (4 g/l). The procedure utilized was as follows:

(i) - a previously weighed amount of starch grains was added to a 250ml beaker and wetted with distilled water under agitation by a magnetic stirrer;

(ii) - to this wetted suspension of starch grains, 40-50ml of a NaOH solution was added slowly. Agitation was maintained to a level sufficient to promote good homogeneizing conditions;

(iii) - a translucid gel was formed;

(iv) - this gel was checked visually for the presence of unreacted starch grains. If grains were observed the preparation was discarded and a new batch was prepared;

(v) - distilled water was then added to dilute the gel to a pre-established concentration. The pH was adjusted to 7 with the addition of HCl;

(vi) - the ratio between starch and NaOH, in a weight basis was kept close to 4:1.
APPENDIX IV - STATISTICAL TREATMENT OF DATA

Most data points presented in this thesis represent an average of at least two tests. For the adsorption test programme the scatter of the data was estimated at +/- 10% for the worst case. In turn, for the flocculation and microflotation test programmes, the deviation from the average value was situated within the +/- 5% range.

The experimental approach taken in the present thesis did not involve any statistical design for experiments. Selection of the test conditions was based upon previous results, analyses of trends and of the previously established objectives.