

**CATALYTIC RECOVERY OF THE OXIDATIVE POWER OF THE CHLORATE  
RESIDUAL IN CHLORINE DIOXIDE DELIGNIFICATION**

**By**

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## **ABSTRACT**

Chlorine dioxide has traditionally been used extensively in the brightening stages of kraft pulp bleaching. More recently, however, environmental pressures have resulted in increased substitution of chlorine dioxide for chlorine in the first bleaching stage, otherwise known as the chlorination or delignification stage. It is now common, in Canadian bleached kraft mills, for the bleach plant to be operated with 100 percent chlorine dioxide substitution in the first stage.

One of the few disadvantages of using chlorine dioxide in the bleaching of chemical pulp is the formation of chlorate. Chlorate formation accounts for up to 30 percent of the chlorine dioxide charge. Since chlorate is inactive as a bleaching chemical, chlorate formation represents a loss in chlorine dioxide bleaching power, and increased bleaching costs. The formation of chlorate has an environmental cost as well. Chlorate is a known fungicide and herbicide, and the chlorate contained in bleached kraft mill effluent has resulted in the elimination of the Bladder Wrack population in the areas surrounding bleached kraft pulp mill outfalls in the Baltic Sea.

The purpose of this study was to examine the potential for vanadium pentoxide to recover the bleaching power of the chlorate residual in the chlorination stage, when the chlorination stage was operated at high substitution. Vanadium pentoxide has been shown to catalyze the transfer of electrons from chlorate to pulp by cycling between the +5 and +4 oxidation states. This catalytic transfer of electrons has loosely been termed the "activation" of the chlorate residual. By "activating" the chlorate residual, we

hoped to decrease the final chlorate concentration and recapture the bleaching power lost as chlorate.

The investigation was conducted using factorial experimental design at two levels. The experimental conditions were chosen to reflect practical bleaching conditions. The experiments were performed using the bag bleaching method with an oxygen delignified pulp. The factors included in the factorial design were temperature, retention time, pH, chlorine dioxide substitution, and vanadium pentoxide charge. In order to measure the "activation" of the chlorate residual, the response of the following variables were measured: final chlorate concentration, brightness, kappa number, pulp viscosity, and pulp physical properties.

The addition of vanadium pentoxide to the chlorination stage had a large impact on the final chlorate concentration. For bleaching runs performed at 80°C, for four hours and at a catalyst charge of 0.005 to 0.01 weight percent, reductions in chlorate concentration of up to 95 % were obtained.

Despite the large drops in chlorate concentration, the addition of vanadium did not substantially increase the oxidizing power of the first bleaching stage. When compared to uncatalyzed bleaching runs at the same temperature, the addition of the catalyst resulted in brightness gains of up to 1 percent. The catalyst had no significant impact on the (D+C)E kappa number of the bleached pulp.

A serious disadvantage of using vanadium pentoxide to "activate" the chlorate residual in chlorine dioxide delignification is the loss in pulp viscosity. The viscosity dropped

from the uncatalyzed values of 22 to 23 cps to as low as 16 cps. These viscosity losses, however, did not result in significant losses in pulp strength properties.

From this study it is recommended that further investigations of recovery of the bleaching power of chlorate in the delignification stage be performed. Of particular interest are organic catalysts for application in closed cycle mills where the solids content of the bleach plant effluent will be fired in the recovery boilers.

Another recommendation focused on the use of vanadium pentoxide for chlorate elimination and effluent improvement. The chlorination stage recycle would be passed through a vanadium pentoxide catalyst stage prior to re-entering the chlorination stage. The vanadium pentoxide could be in the form of plates or immobilized catalyst. This would result in reductions in chlorate concentration in the chlorination stage without entraining vanadium pentoxide in the effluent stream.

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## 1. INTRODUCTION

The kraft pulping process is used globally for the production of high quality chemical pulp. Generally, kraft pulps are chemically treated in pulp mill bleach plants to produce a high brightness final product.

Figure 1.1 illustrates the prevalent bleaching sequence used in Canadian pulp mills (Pryke *et al.* 1993).

As seen in Figure 1.1, chlorine dioxide is used extensively in the bleaching of kraft pulp

**(D, D+C)E<sub>o</sub>DED**

where each bleaching stage is described as follows:

**(D,D+C):** A delignification stage operated with most of the chlorine dioxide (D) added more than 10s before chlorine (C) but with a small amount added with chlorine. This stage focuses on lignin removal.

**E<sub>o</sub>:** An oxygen reinforced alkaline extraction stage

**DED:** The two chlorine dioxide brightening stages separated by an alkaline extraction stage. These stages focus on pulp brightening.

**Figure 1.1: The prevalent bleaching sequence used in Canadian kraft mills (Pryke *et al.* 1993)**

in Canada. The (D,D+C) stage is known as the chlorination or delignification stage.

As the name implies, the purpose of the first bleaching stage is to remove most of the lignin that remains in the pulp when it enters the bleach plant. Although the following two D stages do result in further lignin removal, they focus on pulp brightening through oxidation of the chromophores in lignin (Reeve 1992).

To improve effluent quality and to respond to market demands for pulp bleached without molecular chlorine (ECF bleaching), bleach plants are being operated with higher chlorine dioxide substitution in the first stage. In a recent survey it was reported that 88 percent of the bleach plants in Canada operate at greater than 25% substitution in the chlorination stage, and that an increasing number are operating at 100% substitution (Pryke *et al.* 1993). The survey found that chlorine dioxide substitution is motivated primarily by environmental concerns. The following reasons for increasing chlorine dioxide substitution were reported:

- to decrease AOX (adsorbable organic halide), dioxins, furans, and colour in effluents;
- to decrease dioxins, furans, and organochlorine concentrations in pulp;
- to decrease the acute toxicity of effluent; and,
- to improve market acceptance.

### **1.1. Chlorate Formation**

One of the few disadvantages of chlorine dioxide bleaching is the formation of chlorate ion. The chlorate released in pulp mill effluent has detrimental effects on the receiving

environment and since it is ineffective as a bleaching chemical. chlorate formation represents a loss in bleaching power. Thus, chlorate formation has both environmental and economic implications.

The chlorate ion ( $\text{ClO}_3^-$ ) is a known fungicide and herbicide and therefore presents an environmental threat to the receiving environment (Germgard 1989). The chlorate contained in Swedish bleached kraft mill effluent has resulted in the disappearance of the Bladder Wrack population in areas surrounding pulp mill outfalls in the Baltic Sea (Rosmarin *et al.* 1986). As a result, the Swedish government is currently regulating chlorate emissions from bleached kraft mill effluent in that country.

Since chlorate is unreactive as a bleaching chemical, the formation of chlorate also represents a loss in the bleaching power charged as chlorine dioxide. Chlorate formation accounts for between 10% and 30% of the chlorine dioxide charged (Ni *et al.* 1993). This directly translates into higher chemical costs

Given the implications of chlorate formation, recovery of the bleaching power lost to chlorate offers both environmental and economic rewards. Since chlorine dioxide substitution in the first bleaching stage is increasing, there is significant incentive to recapture the bleaching power of chlorate in this stage.

### **1.2. Recovering the Bleaching Power of the Chlorate Residual**

This work is focused on the recovery of the bleaching power lost as chlorate through vanadium pentoxide catalysis. Vanadium pentoxide has been shown to catalyze the transfer of electrons from chlorate to pulp by cycling between the +5 and +4 oxidation

states (Deutsch *et al.* 1979, Rapson *et al.* 1959). This catalytic transfer of electrons has loosely been termed the "activation" of the chlorate residual, although it is actually vanadium that oxidizes the pulp substrate. By "activating" the chlorate residual, we hoped to address both the environmental and economic implications of chlorate formation.

Previous work has shown that vanadium pentoxide can be used to catalyze the bleaching of kraft pulp with the chlorate ion. "Activating" the chlorate residual in chlorine dioxide brightening resulted in brightness gains, but only at pH values below 3 (Deutsch *et al.* 1979). Since the optimum pH for chlorine dioxide brightening is 4, there is little incentive to add vanadium pentoxide to the brightening stages.

Furthermore, vanadium pentoxide "activation" of chlorate has also been shown to result in serious losses in pulp viscosity (Rapson *et al.* 1979).

This work is based on the "activation" of the chlorate residual in the delignification stage. In terms of the best site for "activating" the chlorate residual, the delignification stage has several advantages over the brightening stages. The pH used in the delignification stage is generally from 2 to 3, which was the pH range found to be most effective for chlorate "activation" (Deutsch *et al.* 1979). And since the pulp in the first stage still contains relatively high lignin concentration, there is a lower requirement for bleaching chemical selectivity than in the brightening stages. The non-selectivity of vanadium pentoxide "activated" chlorate should have a lower impact in the delignification stage than in the subsequent brightening stages.

### **1.3. Objectives of this Work**

Our investigation focused on the impact of vanadium pentoxide addition to the first bleaching stage, operated at high chlorine dioxide substitution. A primary objective of the work was to choose factors and variable settings that reflect prevalent Canadian mill operating conditions, or potentially useful variations of these operating conditions. Since oxygen pre-bleaching is now widely accepted in the industry, we used an oxygen delignified pulp in our experiments.

The variables included in the optimization of catalyzed chlorine dioxide delignification were the

- Degree of substitution,
- pH,
- Time,
- Temperature, and
- Vanadium Charge.

The degree of substitution and the pH were chosen because they are known to have strong impacts on chlorate formation (Ni *et al.* 1993). The retention time, temperature, and catalyst charge were included because of the potential impact on catalyst activity.

The primary goals of the work were as follows:

1. To examine the impact of the catalyst on the final chlorate concentration

2. To measure the increase in bleaching power associated with catalyst addition. The bleaching efficiency was measured through brightness and kappa number determinations.
3. To identify the impact of the catalyst addition on the physical properties of the bleached pulp. The viscosity, strength and optical properties were all measured.



## **2. LITERATURE REVIEW**

The following sections discuss the literature relevant to this work, including the formation and impact of residual oxidants in chlorine dioxide delignification, the aqueous chemistry and catalytic reactions of vanadium pentoxide, and the use of vanadium pentoxide in kraft pulp bleaching.

A detailed review of the literature regarding chlorine dioxide bleaching is beyond the scope of this work. There are many excellent summary papers which discuss the impact of chlorine dioxide substitution on kraft pulp bleaching. The reader is referred to the papers by Ni (1992), Pryke (1992), McCubbin *et al.* (1991), Solomon *et al.* (1993), McCleay *et al.* (1987), and Reeve and Weishar (1991) for thorough discussions of the use of chlorine dioxide in the first stage.

### **2.1. Chlorate Formation**

Significant progress has been made into understanding the mechanism of chlorate formation in kraft pulp bleaching, and the factors which contribute to chlorate formation.

The following sections discuss the residual oxidants in chlorine dioxide delignification, the mechanism of chlorate formation, the impact of chlorate formation on the receiving environment, and the operating conditions which minimize chlorate formation.

#### **2.1.1. Residual Oxidants in Chlorine Dioxide Bleaching**

When chlorine dioxide oxidizes pulp, it is reduced to lower oxidation states. These lower oxidation state chlorine compounds can further react with either the pulp or

other inorganic chlorine species in solution. The inorganic chlorine species that exist following chlorine dioxide bleaching termed "residual oxidants".

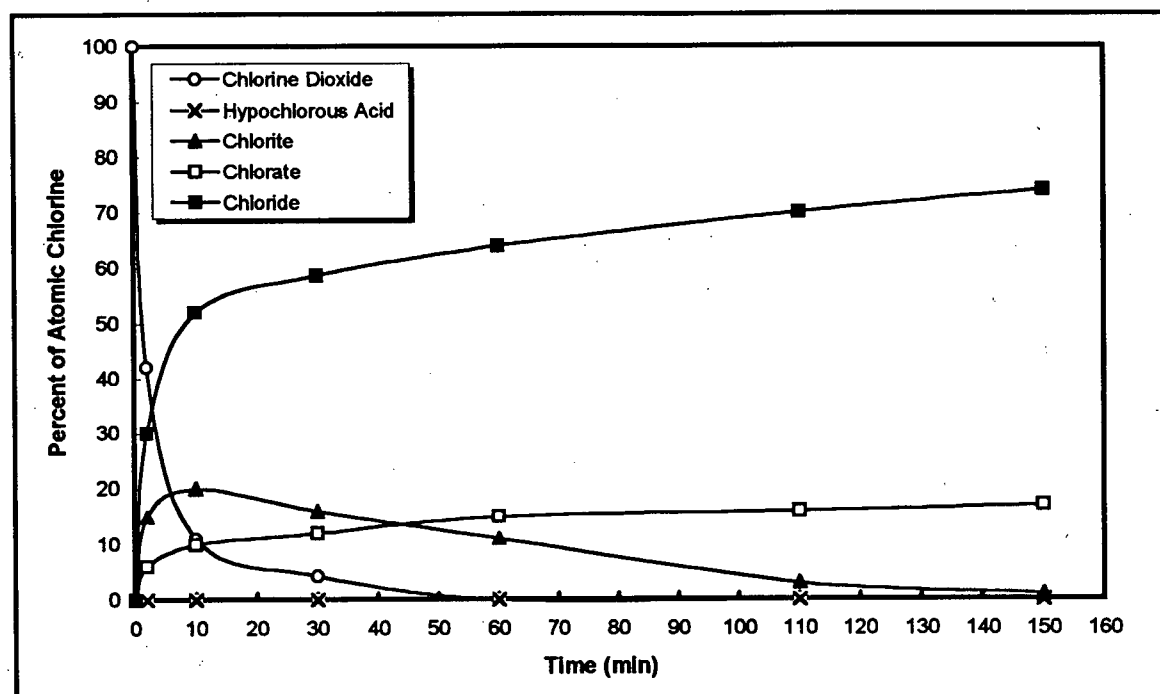
As chlorine dioxide bleaches pulp, it is successively reduced to chlorite ( $\text{ClO}_2^-$ ), hypochlorous acid ( $\text{HOCl}$ ), and chloride ( $\text{Cl}^-$ ). The reduction half reactions are illustrated in Equations 2.1, 2.2, and 2.3.



The inorganic species included in equations 2.1 through 2.3 may also interact to regenerate chlorine dioxide or to form chlorate (Emmenegger and Gordon 1967).

Reaction 2.5 shows that chlorite can react with molecular chlorine to regenerate chlorine dioxide. Reactions 2.4 and 2.6 show that the reaction of hypochlorous acid and chlorite can result either in chlorine dioxide regeneration or chlorate formation.





**Figure 2.1: The concentration profiles for the inorganic chlorine species in pure chlorine dioxide bleaching of kraft pulp at 45°C. (Data from Ni 1992)**

The distribution of the inorganic species, that result from reactions 2.1 through 2.6, has been studied extensively (Reeve and Weishar 1991, Wartiovaara 1985). Typical concentration profiles for the inorganic species produced in chlorine dioxide bleaching are shown in Figure 2.1. The Figure shows that the primary oxidizers, chlorine dioxide and chlorite, were spent after 60 and 150 minutes, respectively. The concentration of chloride, the end product of complete reduction of chlorine dioxide, increased steadily as bleaching proceeded. The concentration of the chlorate ion increased asymptotically to approximately 20 % of the chlorine dioxide charge.

### 2.1.2. The mechanism of Chlorate Formation

Chlorate formation results from the reaction of chlorine dioxide with pulp, followed by a series of inorganic reactions in solution. The following sections discuss the formation of chlorate with respect to both the reaction of chlorine dioxide with pulp, and the reactions of the inorganic chlorine species in the bleaching solution.

#### 2.1.2.1. Chlorate Formation and Pulp Properties

Lindgren and Nilsson (1975) studied the formation of chlorate from the oxidation of nine lignin model compounds with chlorine dioxide. Compounds containing phenolic hydroxyl groups produced the lowest yields of chlorate: between 3 and 5 percent of the oxidizing power of the chlorine dioxide charged. Compounds containing both phenolic hydroxyl and carbonyl groups gave between 10 and 15 percent chlorate. The highest yields, between 12 and 35 percent, came from compounds containing an aliphatic double bond. It was also discovered through some related work that chlorine dioxide preferentially attacks phenolic hydroxyl groups over other functional groups.

Bergnor *et al.* (1987) summarized two pathways in which chlorine dioxide reacts with lignin:

- Path A involves the reaction of chlorine dioxide with phenolic hydroxyl groups. One-half of the chlorine dioxide reacting via this path is reduced to chlorite. In turn, small amounts of chlorite disproportionate to form chlorate, chlorine dioxide and chloride. The other half of the chlorine dioxide that reacts via path A is reduced to hypochlorous acid with no resultant chlorate.
- Path B involves the reaction with carbonyl groups and aliphatic double bonds. Here, one half of the chlorine dioxide is reduced to

hypochlorous acid with no resultant chlorate formation. The other half is directly oxidized to chlorate.

Comparing paths A and B, it is evident that path B produces most of the chlorate generated from the reaction between chlorine dioxide and lignin.

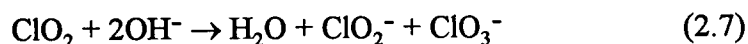
This two path scheme may help to explain why both oxygen and CE pre-bleached pulps produce more chlorate per mole of chlorine dioxide than kraft pulp. Since kraft pulp lignin has a larger proportion of phenolic hydroxyl groups than pre-bleached pulps, more chlorine dioxide reacts via path A, and less chlorate is formed (Farr 1992).

#### **2.1.2.2. The Inorganic Reactions of Chlorate Formation**

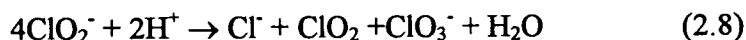
As part of a fundamental study of chlorine dioxide bleaching, Ni *et al.* (1993) identified the inorganic reaction responsible for the formation of chlorate during the chlorine dioxide bleaching of kraft pulp.

The three plausible inorganic reactions that result in chlorate formation are shown below (Ni *et al.* 1993):

1. The disproportionation of chlorine dioxide:



2. The acid catalyzed decomposition of chlorite,



3. The reaction between chlorite and hypochlorous acid.



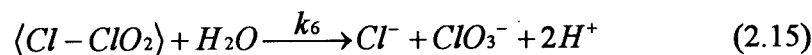
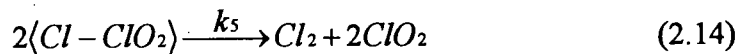
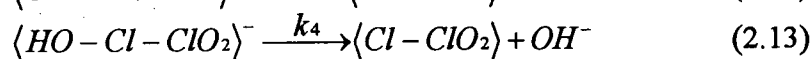
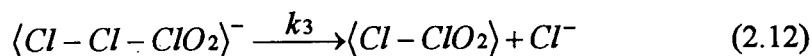
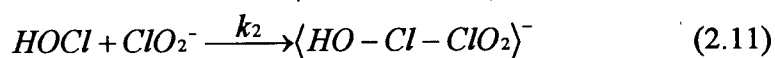
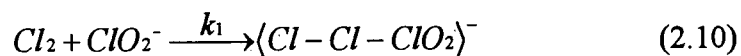
To examine the contribution of reaction 2.7 to chlorate formation, fully bleached pulp was treated with chlorine dioxide. Since no chlorate was detected, Ni *et al.* (1993) concluded that it is the oxidation products of chlorine dioxide that result in chlorate formation and the disproportionation of chlorine dioxide, shown in equation 2.7, is negligible.

To quantify the contribution of chlorite decomposition to chlorate formation, aqueous sodium chlorite was subjected, without pulp, to a pH of 2.5 and a temperature of 45°C for up to 150 minutes. Since no chlorate was detected in the experiments, it was concluded that the chlorate formed from reaction 2.8, the acid catalyzed decomposition of chlorite, could be neglected. This agrees with the summary of information presented by Nilsson and Sjostrom (1974) which concluded that decomposition is only significant if chlorine is present and the pH is greater than 5.

To study the contribution of reaction 2.9 to chlorate formation, Ni *et al.* (1993) used sulfamic acid, a known hypochlorous acid scavenger (Bergnor *et al.* 1987), to effectively remove the hypochlorous acid from solution as it was produced in the bleaching reactions. Since no chlorate was detected, they concluded that the reaction between hypochlorous acid and chlorite must be responsible for chlorate formation.

The mechanism of the reaction between chlorite and hypochlorous acid, shown in Figure 2.2, was first proposed by Taube and Dodgen (1949) and later modified by Emmenegger and Gordon (1967). A discussion of the evidence supporting the reaction mechanism shown in Figure 2.2 is presented by Gordon *et al.* (1972). They conclude that the  $\text{Cl}_2\text{O}_2$  reaction mechanism is consistent with the stoichiometry and rates reported in the literature for the reaction of  $\text{ClO}_2^-$  with  $\text{HOCl}$  and  $\text{Cl}_2$ .

The formation of chlorate is the result of a series of competing reactions. Both of the consecutive reactions 2.10 followed by 2.12, and 2.11 followed by 2.13, result in the formation of the dichlorine dioxide intermediate ( $\text{Cl}_2\text{O}_2$ ). The dichlorine dioxide intermediate then reacts further to form either chlorine and chlorine dioxide through reaction 2.14, or chloride and chlorate through reaction 2.15.



**Figure 2.2: The mechanism of chlorate formation during chlorine dioxide bleaching.**

Gordon *et al.* (1972) examined the existing literature regarding the reactions shown in Figure 2.2 and found agreement between this reaction mechanism and the observed kinetics and stoichiometry of chlorite ( $\text{ClO}_2^-$ ) reactions. In the discussion they suggest that the following conditions will tend to favour chlorine dioxide regeneration through equation 2.14 over chlorate formation via reaction 2.15:

- Shifting the chlorine equilibrium to favour elemental chlorine

Gordon *et al.* (1972) report that increasing the hydrogen ion concentration or increasing the chloride ion concentration tends to favour chlorine dioxide re-generation over chlorate formation. Since, according to equation 2.16, increasing either the hydrogen or chloride ion concentration tends to favour elemental chlorine over hypochlorous acid, they conclude that shifting the chlorine equilibrium towards elemental chlorine reduces chlorate production.





- High dichlorine dioxide intermediate concentration

Emmenegger and Gordon (1967) report that  $k_1$  is greater than  $k_2$ . As a result, shifting the chlorine equilibrium shown in equation 2.16 towards elemental chlorine by decreasing pH or increasing the chloride ion concentration will result in higher concentrations of the intermediate dichlorine dioxide ( $\text{Cl}_2\text{O}_2$ ) species. Furthermore, increasing the hydrogen ion concentration will tend to increase the rate of reaction 2.13, which will also increase the concentration of  $\text{Cl}_2\text{O}_2$ . As a result of these observations, Gordon *et al.* (1972) conclude that increasing the concentration of the  $\text{Cl}_2\text{O}_2$  intermediate tends to decrease chlorate formation relative to chlorine dioxide re-generation.

### **2.1.3. The Impact of Operating Conditions on Chlorate Formation**

Many studies have been performed into the impact of delignification stage operating conditions on the formation of chlorate. The existing information is summarized in sections 2.1.3.1 through 2.1.3.11.

#### **2.1.3.1. Chlorine Dioxide Substitution**

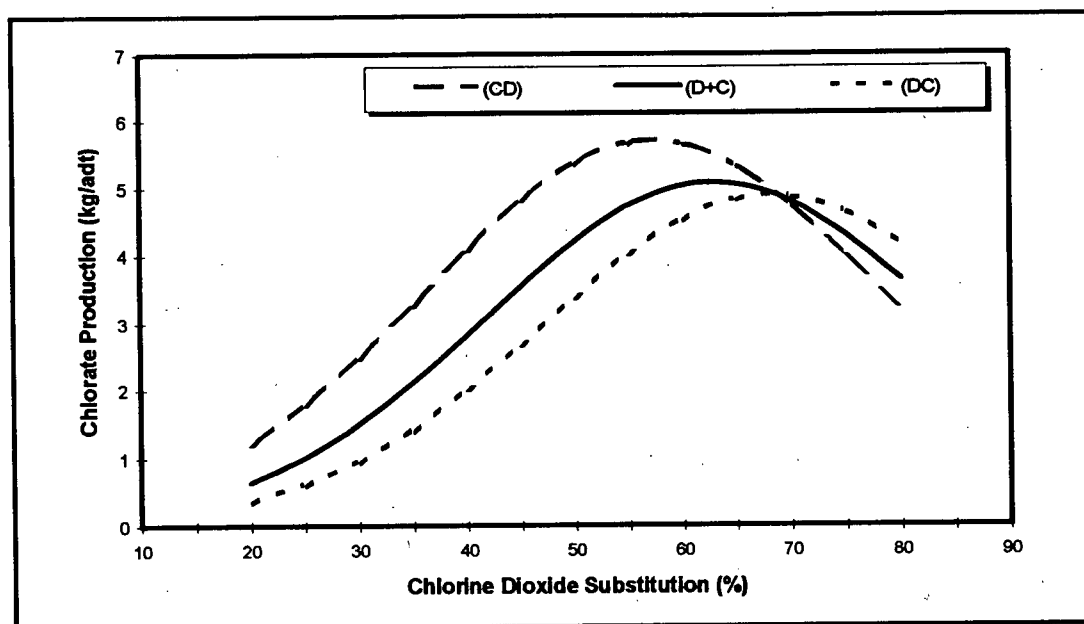
As part of a practical study of the impacts of chlorination stage recycle on effluent quality, Farr (1991) examined chlorate production as a function of substitution. The results of a model fit to Farr's data are illustrated in Figure 2.3. In general, chlorate production increased with substitution. At high levels of substitution, however, a local

maximum was encountered and the chlorate production began to decrease with further increases in substitution.

Farr's results are supported by the summary of existing information presented in Table 2.1. In four of the investigations reported in the Table, a maximum in chlorate production occurred between 70 and 85% substitution. In these instances, chlorate production then decreased as substitution was further increased.

#### **2.1.3.2. Order of Oxidant Addition**

Figure 2.3 also illustrates the findings of Farr (1991) with respect to the impact of order of oxidant addition, or mode, on chlorate production. The Figure shows that the impact of mode on chlorate formation is a function of substitution. The DC mode gave the lowest chlorate formation up to 68 percent substitution. At substitution of greater than 68 percent, the CD mode produced the least chlorate. Simultaneous addition, C+D mode, gave a midrange chlorate production for all substitution cases.



**Figure 2.3: The impact of substitution and mode of addition on chlorate production. (Data taken from Farr 1991)**

Table 2.1 shows that there is limited agreement as to the effect of mode of addition on chlorate production. The addition of chlorine dioxide before chlorate gave the lowest production in all cases except one at 90% substitution (Bergnor *et al* 1987).

Further evidence for the crossing of the chlorate production curves is provided by Nilsson and Sjostrom (1974). In studying the effect on chlorate formation of small amounts of chlorine added to the first chlorine dioxide stage, they found that less chlorate was formed when the chlorine was added before, as opposed to with, the chlorine dioxide. While not directly applicable to the chlorination stage, bleaching in a D stage with 2, 4, and 6 % chlorine substitution as studied by Nilsson and Sjostrom (1974) is somewhat analogous to bleaching in a C stage with 98, 96, and 94 % chlorine dioxide substitution. This tends to corroborate the finding that at high levels of chlorine dioxide substitution, a CD mode yields less chlorate (Bergnor *et al.* 1987).

#### **2.1.3.3. Reaction Time**

Reeve and Wieshar (1991) found that at 50°C chlorate formation was complete after approximately 30 to 40 minutes. This is consistent with the findings of Ni *et al.* (1993) shown in Figure 2.4. Although chlorate formation at 25 °C was complete within 5 minutes, chlorate formation at 45°C required approximately 40 minutes to reach completion. The longer retention time required to reach the final chlorate concentration at 45°C was attributed to increased decomposition of the chlorite in solution, according to Equation 2.8. With increased decomposition of chlorite, more chlorate was formed and a longer time was required to reach the final chlorate concentration at 45°C.

Further data is provided by Kramer (1972), who found that chlorate formation was independent of the reaction times used of 15, 30, and 60 minutes.

#### **2.1.3.4. Bleaching Temperature**

Figure 2.4 illustrates the effect of temperature on chlorate formation (Ni *et al.* 1993). As the temperature was increased from 25°C to 45°C, the percent of the chlorine dioxide charged as chlorate approximately doubled. After 150 minutes, the chlorite accounted for 21.4 percent and 0.9 percent of the atomic chlorine in solution at 25 °C and 45°C, respectively. As discussed in 2.1.3.3, the increase in chlorate formation at 45°C is attributed to the decomposition of chlorite through Equation 2.8.

Reference	Unbleached kappa number (ml)	Kappa factor	Mode	Location of relative maximum (% eq. Cl <sub>2</sub> )	Relative order of chlorate production	Maximum chlorate production (kg/adt)
Kramer (1972)	32.3	0.20	C+D	-	-	2.5 <sup>a</sup>
Reeve and Rapson (1980)	32 <sup>b</sup>	0.16	CD C+D DC	- 70 -	C+D>CD>DC	3.2
Bergnor <i>et al.</i> (1987)	29.3	0.20	CD	70	substitution <60% CD>C+D>DC	5.2 <sup>c</sup>
			C+D	75	substitution 60-90% C+D>CD>DC	
			DC	-	substitution >90% C+D>DC>CD	
Axegard (1987)	17.2	0.20	C+D DC	70 70	C+D>DC	3.0 <sup>c</sup>
Germgard and Karlsson (1988)	17.2	0.18	C+D DC	75 85	C+D>DC	2.2 <sup>c</sup>
Liebergott <i>et al.</i> (1990)	31.2	0.22	CD C+D DC	- - -	CD=C>DC	4.6
Histed <i>et al.</i> (1991)	36.2	0.19	DC	-	-	3.8
Farr (1991)	31.0	0.21	CD C+D DC	- - -	substitution < 68% CD>C+D>DC	5.0
					substitution > 68% DC>C+D>CD	

**Table 2.1: A summary of the literature concerning chlorate formation in the chlorination stage. (expanded from Farr 1991)**

<sup>a</sup> From graphical results at 25°C and pH2.

<sup>b</sup> Converted from a permanganate number of 21 ml.

<sup>c</sup> Pulp moisture not specified

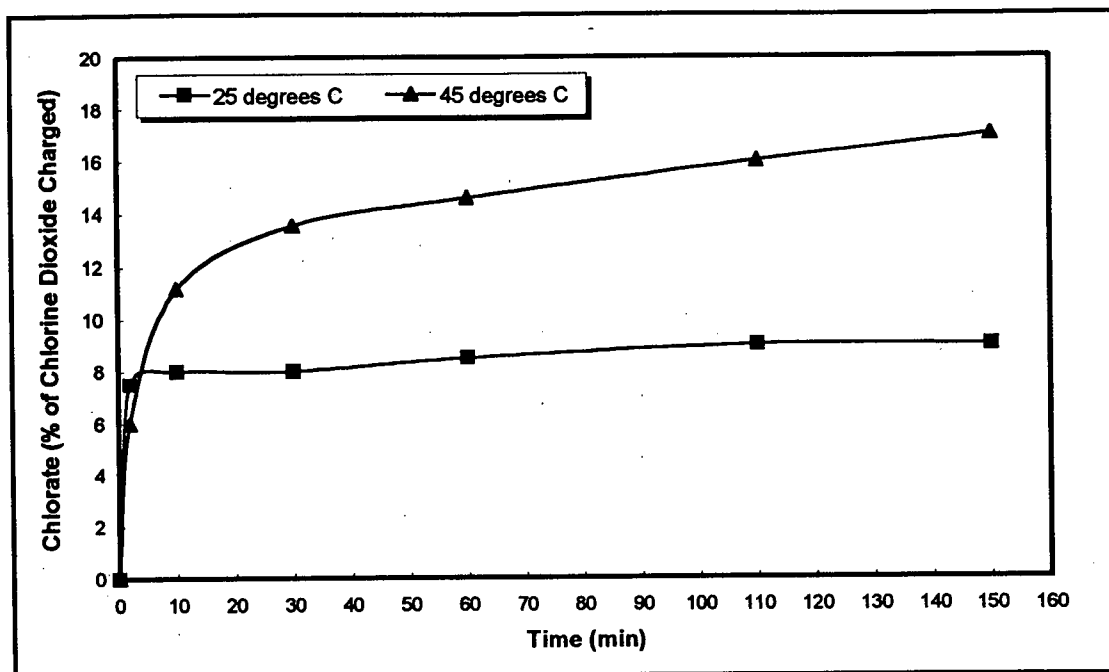
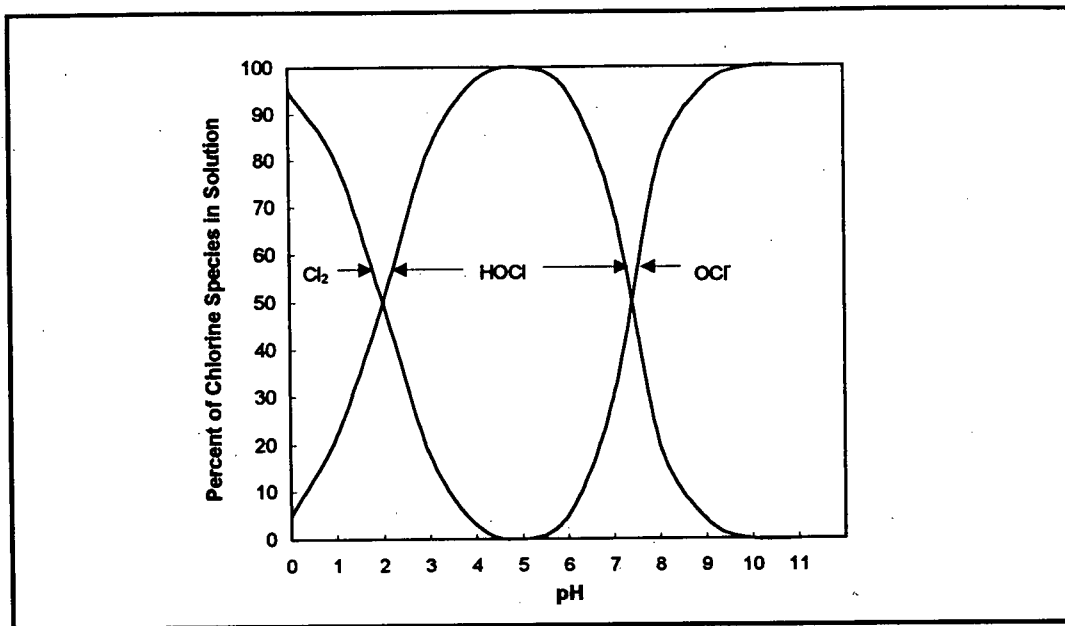


Figure 2.4: The formation of chlorate at 25°C and 45°C. (Data from Ni *et al.*

#### 2.1.3.5. Delignification Stage pH

Generally, chlorate formation is known to decrease with decreasing pH (Wartiovaara 1985).

Ni *et al.* (1993) explained the impact of pH on chlorate production in terms of the chlorate formation mechanism. As seen in Figure 2.5, the chlorine/hypochlorous acid equilibrium is a strong function of pH. Lowering the pH favours molecular chlorine over hypochlorous acid which, according to the discussion in Section 2.1.2.2, results in reduced chlorate formation.



**Figure 2.5: The aqueous chlorine equilibrium distribution (From Smook 1992)**

#### **2.1.3.6. Chlorine Contamination of the Chlorine Dioxide Charge**

Reeve and Weishar (1991) studied the impact of chlorine contamination on chlorate formation for pure chlorine dioxide delignification. They found that runs performed at 95 percent substitution produced the same quantity of chlorate as runs performed at 100 percent substitution and, therefore, chlorine contamination was not a concern. The results were the same for oxygen pre-bleached and unbleached kraft pulps.

Bergnor *et al.* (1987) investigated the impact of chlorine contamination at high levels of substitution. With 70 percent substitution and a DC mode of addition, having 10 % of the available chlorine in the chlorine dioxide solution as chlorine caused a 0.5 kg/adt decrease in chlorate formation. At 30 % percent substitution, the difference between using pure chlorine dioxide and that containing some chlorine was not significant.

### **2.1.3.7. Chlorination Stage Recycle**

As part of a larger investigation of the impact of chlorination stage recycle on effluent quality, Farr (1992) investigated the response of chlorate concentration to recycle. Farr's experiments were performed from a practical perspective, using a laboratory scale simulation of the chlorination stage. It was found that recycle had no significant effect on the production of chlorate.

An earlier study on the effect of effluent recycle on chlorate production was done by Reeve *et al.* (1980). Chlorination effluent recycle was simulated by adding first stage filtrate from a pulp mill to a series of batch laboratory bleaching trials. Both C+D and DC modes of addition were investigated at 70 % substitution. Chlorate production was found to be unaffected by recycle levels of up to 10 percent total organic carbon (TOC) on pulp. Approximate calculations show that the maximum recycle of chlorination filtrate possible industrially corresponds to 2 percent TOC on pulp. The mill effluent was concentrated by vacuum evaporation enabling this value to be surpassed.

### **2.1.3.8. Pulp Consistency**

The production of chlorate during chlorine dioxide bleaching is decreased as consistency increases (Reeve and Weishar 1991, Ni 1992). Ni *et al.* (1993) explained the impact of consistency using the chlorate formation mechanism discussed in Section 2.1.2.2. As consistency is increased, the concentrations of all species, including the dichlorine dioxide intermediate, are increased. Since higher dichlorine dioxide



concentrations favour chlorine dioxide regeneration over chlorate formation, less chlorate is formed at higher consistency.

#### **2.1.3.9. Oxidant Charge**

The initial oxidant charge is a function of the kappa number of the incoming pulp; pulps with higher incoming kappa numbers require higher oxidant charges to reach a target bleached kappa number. Oxygen delignified pulps usually have a kappa number in the range of 16 to 19, while unbleached pulps tend to have kappa numbers closer to 30. As a result, higher oxidant charges are used for unbleached kraft pulps.

The fraction of the oxidant charge that is lost as chlorate is higher for oxygen pre-bleached pulps (McDonough *et al.* 1985). Ni *et al.* (1993) explained the higher fraction of chlorate formation with oxygen delignified pulps according to the chlorite/hypochlorous acid formation mechanism. At the reduced kappa number, less lignin is available for the fast reaction with the chlorine/hypochlorous acid equilibrium pair. This means that more chlorine/hypochlorous acid is available for chlorate formation, and a higher fraction of chlorine dioxide is lost as chlorate.

Naturally, unbleached kraft pulp will require a much higher oxidant charge than an oxygen delignified pulp and the chlorination stage effluent will contain higher loadings of chlorate.

#### **2.1.3.10. Chloride Ion Concentration**

Several studies have reported that increasing the chloride ion concentration in the bleaching liquor reduces chlorate production (Germgard, Teder and Tormund 1981,

Reeve and Weishar 1991). Ni *et al.* (1993) concluded that this effect is due to the shifting of the chlorine/hypochlorous acid equilibrium, shown in equation 2.16, towards elemental chlorine. Since the chlorate formation reaction is believed to result from reaction of chlorite and hypochlorous acid, this favours chlorine dioxide regeneration over chlorate formation (see section 2.1.2.2).

#### **2.1.3.11. The Impact of Chlorate Formation on the Receiving Environment**

Chlorate is a known fungicide and herbicide and when contained in BKME, chlorate has the potential to seriously affect the aquatic plant life in the receiving environment (Isensee *et al.*, 1973).

Chlorate discharges in BKME in Sweden have been linked to the disappearance of Bladder Wrack (*Fucus vesiculosus*), a brown algae, in the Baltic Sea (Rosmarin *et al.*, 1986, Germgard 1989). In one instance, the Bladder Wrack population within a 12 km<sup>2</sup> area surrounding the bleached kraft mill outfall was destroyed. Since the areas containing brown algae, and especially Bladder Wrack, are important breeding areas for a variety of aquatic organisms, the disappearance of the algae impacts heavily on the surrounding ecosystem.

Rosmarin *et al.*, (1986) studied the impact of chlorate on a bladder wrack population that was transplanted to an artificial environment. The results indicate that chlorate hinders the growth of bladder wrack at concentrations as low as 20 µg/l, which corresponds to a dilution factor in the pulp mill effluent of 1000 to 2000. Simulation of

the conditions and chlorate concentrations found in Swedish BKME receiving environments showed that it takes approximately 2 months for the chlorate to disappear.

The impact of chlorate on freshwater river systems was studied by Perrin and Bothwell (1992). It was found that chlorate concentrations typically found in pulp mill receiving environments did not reduce the specific growth rates or the population distribution of freshwater diatoms, and that chlorate discharges from bleached kraft mills (BKM) would not affect the riverine algal community.

#### **2.1.4. Reduction of Chlorate during Effluent Treatment**

Germgard (1989) investigated the potential of reducing chlorate produced in the bleach plant through biological or chemical treatment.

Anaerobic biological reactions during secondary treatment of pulp mill effluent can reduce chlorate to chloride. Aerated lagoon treatment systems often have regions of low oxygen concentration, especially in the sediment at the bottom of the lagoon.

These regions provide anaerobic zones where facultative organisms can digest and reduce the chlorate contained in the effluent stream. If the aerated lagoon is operated with no initial aeration at a pH of 7, chlorate degradation occurs within 5 to 10 hours.

The elimination of chlorate from effluent treated in aerated lagoon systems is supported by studies performed by Munro *et al.* 1990, and Pryke *et al.* 1993. These studies found that the chlorate levels in bleached kraft mill effluent (BKME) from mills employing aerated lagoon secondary treatment systems were below detection limits.

Although , chlorate appears to be effectively treated in aerated lagoons, chlorate reduction does not occur in activated sludge systems. Activated sludge systems do not provide the facultative zones required for biological reduction of the chlorate contained in the effluent stream. As a result, effluent discharges from activated sludge systems may contain chlorate.

The use of chemical reducing agents is another viable treatment for chlorate. The reduction of chlorate is most easily performed using sulfur dioxide since it is readily available at bleached kraft mills. Other chemical treatments include iron chloride or iodine. The application of 3 mol of sulfur dioxide for each mol of chlorate, at pH 2 and 50 to 60°C with a retention time of at least one hour can completely eliminate the chlorate contained in the bleach plant effluent. Germgard (1989) suggests that a mill effluent pipe is a suitable reactor, provided the retention time is sufficient.

## **2.2. Vanadium Pentoxide**

Vanadium pentoxide was the catalyst used for the oxidation of the chlorate residual in the current work. The oxidation states of vanadium range from -I to +V (Lee 1991).

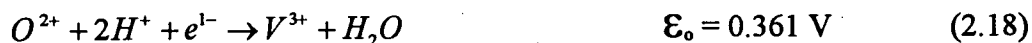
Vanadium pentoxide is in the +V oxidation state.

Vanadium pentoxide is a brick red powder that is soluble in aqueous solutions at 0.07 g/l. It is completely soluble in strongly acidic and basic solutions.

As shown in equation 2.17, vanadium in the +V oxidation state is a mildly good oxidizing agent with a standard reduction potential of 1.000 volt (Lee 1991).



When involved in oxidation reactions, vanadium is reduced to the +IV state. In aqueous solutions, vanadium in the +IV oxidation state exists as the stable vanadyl ion ( $VO^{2+}$ ). Mildly to strongly acidic solutions of the vanadyl ion are stable for months. With the standard reduction potential of 0.361 illustrated in equation 2.18, the vanadyl ion is a poor oxidizer (Lee 1991).



The following sections discuss the catalytic reactions, the kinetics of vanadium oxidations, and the aqueous chemistry of the vanadium species.

### 2.2.1. Vanadium Pentoxide Catalysis

Vanadium pentoxide is an important catalyst for industrial oxidation reactions. Among the important reactions that are catalyzed by vanadium pentoxide are the following (Lee 1991, Sidgewick 1950):

- oxidizing sulfur dioxide to sulfur trioxide in the contact process for sulfuric acid production,
- oxidizing naphthalene to phthalic acid,
- oxidizing toluene to benzaldehyde,

- sulfonizing hydrocarbons and pyridine,
- oxidizing stannous salts by stannous or chloric acid,
- oxidizing cyclic organic compounds with hydrogen peroxide, and
- oxidizing sugar with nitric acid.

Studies of these reactions show that pentavalent vanadium reactions predominantly proceed through 1 electron transfer reactions (Waters and Littler 1965). Thus, vanadium pentoxide catalysis results in free radical formation.

### **2.2.2. Vanadium Pentoxide Oxidations of Organic Compounds**

Littler and Waters (1959) performed a semi-qualitative mechanistic study of the oxidation of acids, aldehydes, ketones, alcohols, phenols, ethers, olefins, and nitrogen compounds with vanadium pentoxide and acidic aqueous solutions. The induced polymerization of vinyl cyanide and the induced reduction of mercuric chloride were used to indicate free radical production during the oxidation reactions. In all cases there was evidence of free radical activity. They concluded that although competing ionic reactions exist, the free radical mechanism predominates in the oxidation of organic compounds with vanadium pentoxide.

In a series of investigations of vanadium pentoxide oxidations of organic compounds in acetic acid solutions, Radhakrishnamurti and Devi (1975), Radhakrishnamurti and Pati (1970), and Radhakrishnamurti and Pati (1969a, 1969b) concluded that the ionic oxidation mechanism predominated.

It appears that the two competing reaction mechanisms (i.e. free radical versus ionic) are a strong function of the solution conditions.

### **2.2.3. Kinetics of Vanadium (V) Oxidations**

Several studies of the kinetics of pentavalent vanadium oxidations of organics have been performed by Radhakrishnamurti and co-workers. Most of Radhakrishnamurti's work was performed in aqueous acetic acid solutions, and so has no direct relevance to the current work.

A summary of the reaction conditions and rate constants found by Radhakrishnamurti is presented in Table 2.2. The Table is intended to illustrate the wide range in rate constant values obtained for vanadium oxidations of organic compounds. The rate of vanadium oxidations of organic substrates in acetic acid solutions is a strong function of temperature, acidity, and solution composition.

### **2.2.4. Aqueous Solutions of Vanadium in the +IV and +V Oxidation State**

The two oxidation states of vanadium that are of interest in the current work are the +IV and the +V states.

The +IV oxidation state is present in aqueous solution as the stable  $\text{VO}^{2+}$  species, commonly known as the vanadyl ion. The  $\text{VO}^{2+}$  is soluble in aqueous solution where it exists as the  $\text{VO}(\text{H}_2\text{O})_5^+$  species (Clark 1973).

Reference	Substrate	Solution Composition (v % Acetic Acid)	Temperature (°C)	Acidity (N - H <sub>2</sub> SO <sub>4</sub> )	Second Order Rate Constant (l·mol <sup>-1</sup> ·min <sup>-1</sup> )
Radhakrishnamurti and Devi (1975)	Cyclic Ketones	10	60	1.0	0.06-0.29
		30	60	2.0	0.20-1.14
		30	60	1.0	0.14-0.75
Radhakrishnamurti and Panda (1970)	Phenols	50	30	0.025/0.075	0.30/0.50 <sup>a</sup>
			40	0.025	0.53
		70	30	0.025	0.59
			40	0.025	0.84
Radhakrishnamurti Pati (1969a)	Cyclic Alcohols	50	40	4.1	0.13 <sup>b</sup>
			60	4.1	0.42
			60	5.4	1.79
Radhakrishnamurti and Pati (1969b)	Halogenated Toluenes	50		8.1	0.003 <sup>c</sup>
			50	10.8	0.07
			70	8.1	0.38
		70	50	8.1	0.03
			70	8.1	0.37

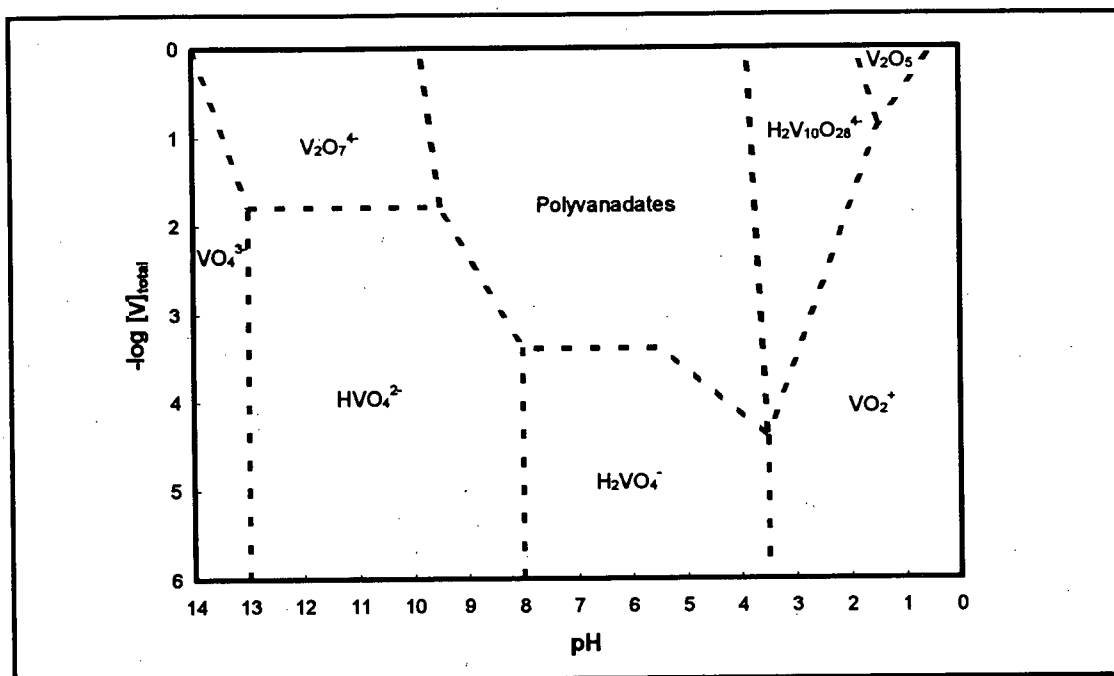
**Table 2.2: A summary of the literature concerning vanadium pentoxide oxidations of organic substrates.**

<sup>a</sup> Rate constant values shown are for phenol.

<sup>b</sup> Rate constant values shown are for cyclohexanol

<sup>c</sup> Rate constant values shown are for chlorotoluene.





**Figure 2.6: The distribution of vanadium (+5) in aqueous solution. (Data taken from Clark 1973)**

Figure 2.6 illustrates the complex aqueous chemistry of the +V oxidation state of vanadium.

The species distribution is a complex function of the total vanadium concentration and the pH of the solution (Lee 1991, Clark 1973). At very high pH values, the vanadium is in the form of the orthovanadate ion  $\text{VO}_4^{3-}$ . As the pH is lowered, the ions polymerize to form polyvanadates. As the pH is lowered below 3, the polymers dissolve and the pentavalent vanadium is present in the  $\text{VO}_2^+$  form.

### 2.3. Vanadium Pentoxide "Activation" of Chlorate

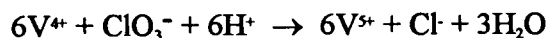
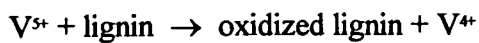
Vanadium pentoxide has been used in previous studies to "activate" chlorate in acidic solutions.

Morioko (1981) patented the use of vanadium pentoxide, alone or in combination with other metal complexes, to reduce the acidity required to produce chlorine dioxide through "activation" of the chlorate in the generator solution.

Marpillero (1957) patented the use of a vanadium pentoxide "activated" chlorate bleaching process that lowered the acidity required for chlorate bleaching. The catalytic bleaching process was operated at pH 2 and a temperature of 70°C for 3 to 4 hours. Marpillero (1958) claimed that brightness gains of 5 to 15 percent over comparable chlorine and hypochlorite bleaching processes could be realized.

Investigation of the pulp properties resulting from the use of "activated" chlorate in pulp bleaching showed that under practical bleaching conditions with a pH of 2, a temperature of 70°C and a four hour retention time, there was serious hydrolytic attack on cellulose (Rapson *et al.* 1959). The losses in cellulose integrity have precluded the use of "activated" chlorate on an industrial scale.

Deutsch *et al.* (1979) investigated the potential of using vanadium pentoxide to "activate" the chlorate residual in chlorine dioxide brightening of kraft pulp. They found that a vanadium pentoxide charge of approximately 0.008 weight percent on oven dry pulp provided the optimum chlorate "activation". In their patent, Deutsch and Shoemaker (1977) noted that the optimum temperature for the chlorate "activation" is between 70°C and 80°C and that brightness increases with increasing temperature, longer retention times, higher catalyst charge, and lower pH.



**Figure 2.7: The mechanism of the vanadium catalyzed bleaching reaction.**

Deutsch *et al.* went on to compare the vanadium catalyzed bleaching system to conventional chlorine dioxide brightening. Brightness reversion and residual chlorate concentrations were reduced at all pH values. They found that the addition of catalyst increased brightness at pH values from 1 to 3, but no brightness gain was noted at higher pH values. Since the optimum pH for chlorine dioxide brightening is around 4, they concluded that there is little incentive to use vanadium pentoxide to recapture the bleaching power lost to chlorate in the brightening stages.

### 2.3.1. The Mechanism of the Catalytic Reaction

The catalytic pulp bleaching reactions are believed to proceed through the vanadium cycling mechanism illustrated in Figure 2.7 (Deutsch *et al.* 1979, Rapson *et al.* 1959, Marpillero 1958).

The vanadium transfers electrons from the chlorate in solution to oxidize the pulp. It does not result in regeneration of chlorine dioxide from chlorate; rather, the bleaching power lost to chlorate is recaptured as pentavalent vanadium oxidations of the pulp.

### **3. EXPERIMENTAL**

#### **3.1. Experimental Design**

The experiments were designed using factorial design at two levels. The entire experimental program consisted of two sets of  $2^4$  factorial designs. The first set of experiments focused entirely on the reduction in chlorate concentration obtained. The second experimental set was designed to examine the impact of the catalytic bleaching system on the bleaching efficiency and the pulp properties in addition to the reduction in chlorate concentration.

A discussion of the choice of factor variables, the response variables used, the levels chosen for each factor variable setting, and a summary of the experimental runs performed is provided in the following sections.

A detailed discussion of factorial design at two levels is beyond the scope of this report. The reader is referred to the paper in Appendix C for an overview of factorial design methods.

##### **3.1.1. Factor Variables**

The operating variables which are known to impact on the quantity of chlorate formed are pH, temperature, the degree of chlorine dioxide substitution, the chloride ion concentration, the size of the oxidant charge, the consistency of the pulp suspension, and the type of pulp used.

Catalytic processes are strongly affected by the concentration of both the catalyst and the substrate, and the temperature of the reaction.

Since the pumping capabilities of most pulp mills in Canada limit the chlorination stage consistency to 3.5 % (Lee 1994), this consistency was used throughout the experimental program.

The impact of chloride ion concentration on chlorate formation is small and it was not considered in the experimental design.

Environmental concerns have caused a decrease in the oxidant charge used in the chlorination stage. The oxidant charge is commonly expressed as the kappa factor, which is determined according to equation 3.1.

$$\text{Unbleached kappa number} \times \text{kappa factor} = \% \text{ Equivalent Cl}_2 \text{ Applied} \quad (3.1)$$

When the kappa factor is increased beyond 0.15 to 0.20, laboratory results have shown that the concentration of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF) increase sharply (Berry *et al.* 1989). To simulate conditions under which the formation of 2,3,7,8-TCDD and 2,3,7,8-TCDF are minimized, a kappa factor of 0.15 was chosen for the experiments performed.

The remaining factors affecting chlorate formation and the activity of the catalyst were used in the experimental design. The first factorial design (Experimental Program 1) included pH, temperature, the degree of substitution, and the catalyst charge. The factor variables

used in the second set of experiments (Experimental Program 2) were the degree of substitution, reaction time, catalyst charge, and temperature.

Mode was not included as a factor variable because of practical difficulties. The addition of bleaching chemicals in the bag bleaching method is cumbersome, and the timing of sequential oxidant addition would be extremely difficult to control.

### **3.1.2. Summary of Runs**

Tables 3.1 and 3.2 illustrate the factor level settings used in Experimental Programs 1 and 2, respectively. The first set of factorial runs performed included the degree of chlorine dioxide substitution, pH, temperature, and catalyst charge as factor variables.

The results of Experimental program 1 were used to identify the effect of each of the factors on the final chlorate concentration. These results were used to design Experimental Program 2. The factors included in the second design were the degree of chlorine dioxide substitution, temperature, time, and catalyst charge.

In addition to the factorial design runs outlined in the tables, blank runs were performed in order to compare the overall performance of the catalyzed bleaching runs to runs without catalyst. A summary of these runs is shown in Table 3.3. The purpose of these runs was to provide a comparison between the impacts of the uncatalyzed and catalyzed bleaching runs on the chlorate concentration, as well as the properties of the pulp produced. Two runs were also performed at 45°C to provide a benchmark for comparing the catalyzed system with conventional delignification.

### **3.1.3. Response Variables**

The purpose of Experimental Program 1 was to investigate the impact of the degree of substitution, pH, temperature, and catalyst charge on the final chlorate concentration.

Chlorate concentration was the only response variable.

The intent of Experimental Program 2 was to follow up the first experimental program with an investigation of the impact of the catalytic system on the bleached pulp properties. Thus, in addition to chlorate formation, the response of the brightness, kappa number, viscosity, and pulp strength and optical properties was measured for each of the runs shown in Table

3.2.

Run	Substitution	Catalyst	Temperature	pH
1	0	0	0	0
2	+	-	+	-
3	-	+	-	-
4	-	+	+	+
5	+	+	-	+
6	0	0	0	0
7	-	+	-	+
8	-	+	+	-
9	+	+	+	-
10	+	-	-	-
11	-	-	+	+
12	-	-	+	-
13	+	-	+	+
14	0	0	0	0
15	+	+	-	-
16	-	-	-	+
17	+	-	-	+
18	-	-	-	-
19	+	+	+	+
20	0	0	0	0

**Table 3.1: Factor level table for Experimental Program 1.**



Run	Substitution	Catalyst	Temperature	Time
1	0	0	0	0
2	+	-	+	+
3	+	+	-	-
4	-	-	+	-
5	+	-	-	-
6	-	+	+	+
7	-	-	-	-
8	+	-	+	-
9	0	0	0	0
10	+	+	+	+
11	-	+	-	-
12	-	+	-	+
13	+	+	+	-
14	+	-	-	+
15	-	-	-	+
16	-	-	+	+
17	+	+	-	+
18	-	+	+	-
19	0	0	0	0

Table 3.2: Factor level table for Experimental Program 2.

Substitution (% eq. chlorine)	Temperature (°C)	Retention Time (min)
50	40	120
	70	120
	80	120
75	75	120
100	40	120
	70	120
	80	120

Table 3.3: A summary of the uncatalyzed bleaching runs.

### **3.2. Materials and Methods**

#### **3.2.1. The Bleaching Runs**

The bleaching runs were performed using the bag bleaching method (Hatton 1966, Hatton 1967). A detailed discussion of the bleaching method used is provided in Appendix A.

The required amounts of pulp, water, and vanadium pentoxide catalyst (added as an aqueous solution) were sealed in the bag. A clamp was placed across the bag to create an empty compartment. The chlorine and chlorine dioxide were charged, via syringe, into the empty section and the bag was resealed.

The bleaching reaction was initiated by removing the clamp and thoroughly mixing the pulp and bleaching chemicals. Once mixed, the bag was placed in a constant temperature bath. The bag was removed from the water bath and kneaded every 20 minutes, to provide mixing of the pulp and oxidants.

#### **3.2.2. The Pulp Source**

In order to simulate a contemporary bleaching reaction, an oxygen delignified pulp was used for the bleaching reactions. A never dried spruce-pine-fir furnish was provided by Cariboo Pulp. The pulp had an initial Kappa number of 17.1, which is in the normal range for an oxygen delignified pulp.

#### **3.2.3. Vanadium Catalyst Preparation**

The vanadium catalyst was charged as an aqueous solution of 0.05 g/l vanadium pentoxide.

The solubility of vanadium pentoxide in water at 20°C is 0.08 weight percent (CRC 1982).

Vanadium pentoxide is completely soluble in acid and alkaline solutions.

Although the solution used in the bleaching runs was below the saturation limit of vanadium pentoxide, the dissolution of vanadium pentoxide in water did not occur at an appreciable rate. As a result, the vanadium pentoxide solution was prepared using water adjusted to pH 12 with sodium hydroxide.

#### **3.2.4. Chlorine Solution Preparation**

An aqueous chlorine solution was formed by absorbing gaseous elemental chlorine in de-ionized water. The concentration of the chlorine solution was determined using the iodometric titration found in CPPA standard method J.22P.

#### **3.2.5. Chlorine Dioxide Generation**

Chlorine dioxide was generated by acidifying sodium chlorite with 10N sulfuric acid. The gaseous chlorine dioxide produced was passed through two flasks containing dilute sodium chlorite solutions to convert any entrained chlorine to chlorine dioxide. The pure chlorine dioxide was absorbed in cold deionized water to produce the chlorine dioxide solution used in the bleaching runs. This solution was stored for up to one month. A detailed discussion of the chlorine dioxide generation system is presented in Appendix B.

To determine the chlorine dioxide concentration, a 10 ml aliquot of chlorine dioxide was pipetted below the surface of a mixture of 40 ml of water and 10 ml of 10% potassium iodide solution. The chlorine dioxide concentration was then determined using the

iodometric titration found in the CPPA standard method J.14P (1966-) for chlorine dioxide plant analysis.

### 3.2.6. Bleached Pulp Property Testing (CPPA 1966-)

The pulp property tests for the bleached pulps were performed in accordance with the CPPA standard testing methods (CPPA 1966-). All of the testing was performed at the PAPRICAN Vancouver laboratory. Table 3.4 shows the standard methods and the instruments used in the pulp and paper tests.

### 3.2.7. Bleaching Liquor Analysis

The residual oxidants potentially present in the bleaching liquor were chlorine, hypochlorous acid (HOCl), chlorine dioxide, chlorite ( $\text{ClO}_2^-$ ), and chlorate.

Pulp Property Test	CPPA standard test method	Instrument Used
Cupriethylene diamine Viscosity	G.24P	
Kappa Number	G.18	Radiometer KTS1 Kappa number system
Brightness	E.1	Technibrite Micro TB-1C
Tear strength	D.9	TMI Tear Tester 800g Pendulum
Breaking Length	D.6H	Instron model 4202
Zero span tensile strength	Useful method D.27U	Pulmac - The Troubleshooter
Burst strength	D.8	The Mullen Tester
Bulk	D.5H	TMI series 400 tester
Opacity	E.2	Technibrite Micro TB-1C

**Table 3.4: A summary of the pulp testing methods used in this study.**

The reactions between pulp and chlorine, hypochlorous acid, and chlorine dioxide are known to proceed rapidly. The chlorite produced in the reactions between cellulosic pulp and chlorine dioxide is completely reacted after 2 hours at 45°C. Since temperatures higher than 70°C were used in this work, the chlorine, chlorine dioxide, chlorite and hypochlorous acid were completely consumed before the reaction was terminated. This was confirmed using the analytical methods found in Rapson and Anderson (1966).

Chlorate was the only residual oxidizing species detected in solution following the bleaching runs.

#### **3.2.7.1. Chlorate Analysis**

The chlorate concentration was determined using the method given by Rapson and Anderson (1966). The accuracy of the method was verified using chlorate solutions in the concentration range found in the bleaching liquor.

At the completion of the desired reaction time, the bags were cooled under cold running tap water for at least 10 minutes. The bleaching liquor was then separated from the pulp and screened. Replicate 100 millilitre samples were pipetted into 500 ml Erlenmeyer flasks. To each sample was added 10 ml of 10 % NaBr and 100 ml of concentrated hydrochloric acid (Fischer scientific reagent grade). The sample was promptly stoppered and allowed to stand for at least 10 minutes.

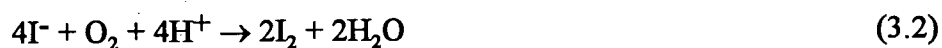
At the completion of the 10 minute period, the iodometric titration was performed. Due to the oxidation by air of iodide to iodine in highly acidic solutions, a small amount of sodium bicarbonate (approximately 300 mg) was added to the sample prior to iodide addition. This

displaced the air in the flask through evolution of carbon dioxide (Vogel 1978). 10 ml of 10 % potassium iodide solution was added to the flask and the iodine liberated was titrated immediately, to the starch end point, with 0.0100 N sodium thiosulphate solution.

### **3.2.7.2. The Air Oxidation of Iodide to Iodine during Chlorate Determination**

A major source of error in the iodometric determination of chlorate concentration is the air oxidation of iodide to iodine (Skoog and West 1980, Vogel 1978).

The reaction proceeds as follows:



The rate of this reaction becomes appreciable in solutions of greater than 0.4 to 0.5 normal acid. Since the chlorate titration is performed in 8N acid, the oxidation of iodide by this mechanism is an important source of error.

The oxidation of iodide is minimized through the use of the bromide intermediate in the chlorate titration. The standard half cell reduction potentials for bromine and iodine are 1.0873 V and 0.5355 V, respectively, indicating that bromide is less easily oxidized than is iodide. As a result, the air oxidation of bromide is negligible in the determination of chlorate concentration. When the iodide is added to the solution, it is readily oxidized to iodine by the bromine in solution. This iodine must be titrated immediately to minimize air oxidation of iodide.

The oxidation of iodide by oxygen in the surrounding atmosphere during the iodine determination is minimized by adding a small amount (300 mg) of sodium bicarbonate to the

solution at various times throughout the titration. This results in the evolution of carbon dioxide and reduces the oxygen concentration in the atmosphere over the solution.

#### 4. RESULTS AND DISCUSSION

The purpose of the experimental program was to investigate the impact of adding vanadium pentoxide to the delignification stage. The investigation was performed in two stages, each consisting of a  $2^4$  factorial design at two levels. The two experimental programs are outlined in Table 4.1.

The first set of experiments, Experimental Program 1, focused on the impact of vanadium pentoxide on the residual chlorate concentration. The factors considered were temperature, pH, substitution, and catalyst charge. As seen in Table 4.2, the results showed that maintaining high temperature and high catalyst charge was the most effective means of minimizing the residual chlorate concentration. The starting pH and the degree of substitution had a large impact on the

##### Interpreting Factorial Design Data

The basis of factorial experimental design is the development of a mathematical expression to fit the response of the system to changes in the factor variables.

We used the following second order model to describe the system:

$$Y = b_0 + \sum_{i=1}^n b_i X_i + b_{12} X_1 X_2 + b_{13} X_1 X_3 + \dots + b_{34} X_3 X_4$$

The terms in the model are described as follows:

$Y$ : the measured response in the system.

$X_i$ : the factor setting for variable  $i$ .

$b_i$ : the coefficient for the main effect of variable  $i$ .

$b_i b_j$ : the coefficient for the interaction effect of variables  $i$  and  $j$ .

(For a detailed discussion of factorial design, see Appendix C.)



Stage of the work	Factor Levels (low/high)				
	pH	Temperature (°C)	Substitution (% Eq. Cl <sub>2</sub> )	Catalyst Charge (weight %)	Time (min)
Experimental program 1	2/4	70/80	50/100	0.001/0.01	-
Experimental program 1	-	70/80	50/100	0.005/0.015	120/240
Uncatalyzed runs	2/4	70/75/80	50/75/100	-	120

**Table 4.1: A summary of the experimental programs.**

formation of chlorate in solution, but had little effect on the final chlorate concentration.

Following the findings of Experimental Program 1, the second experimental program was designed. Experimental Program 2 was designed to optimize the reduction in chlorate concentration obtained, and to investigate the impact of chlorate "activation" on bleaching efficiency and pulp properties. Since it was shown to have little effect in the first phase, pH was dropped from experimental program 2. In its place, the impact of delignification stage retention time was added. To maximize the chlorate reductions obtained, the catalyst charge was increased for this set of experiments. The temperature could not be increased beyond 80°C due to unacceptable viscosity losses.

In many cases, the results of the catalyzed runs were compared to the results from the uncatalyzed runs. All such comparisons to catalyzed bleaching runs were made with uncatalyzed bleaching runs at the same temperature, substitution, and pH. In order to provide a reasonable comparison to standard industrial delignification, the uncatalyzed runs had retention times of 2 hours.

A discussion of the impact of vanadium pentoxide addition on chlorate concentration, bleaching efficiency, and bleached pulp properties is presented in the following sections.

The results are interpreted using factorial analysis.

#### **4.1. The Response of the Residual Chlorate Concentration**

Since the chlorate concentration is the most direct measure of the catalyst activity, the final chlorate concentration was included in both factorial designs. The factor settings and the chlorate concentration responses for experimental programs 1 and 2 are summarized in Tables 4.2 and 4.3, respectively.

A discussion of the impact of the factor variables on the chlorate in solution is presented in the following sections.

The impact of the factor variables on the chlorate concentration is reported in two ways: the effect on the final chlorate concentration and the percent reduction in chlorate concentration. The percent reduction is a comparison of the final chlorate concentration in

#### **Interpreting Main Effects in Factorial Design**

Mathematically, the main effect may be expressed as follows:

$$\text{Main Effect of Variable } i = \Delta Y = b_i \Delta X_i$$

A large main effect shows that increasing the factor setting of variable  $i$  has a large impact on the response of  $Y$ . If the main effect is negative, then increasing  $X_i$  tends to decrease  $Y_i$ .

For example, the data in 4.2 shows that the main effect of temperature on the residual chlorate concentration is -0.240 mM. Therefore, the statistical analysis showed that the average impact of increasing the temperature from 70°C to 80°C was to decrease the chlorate concentration by 0.240 mM.

catalyzed and uncatalyzed bleaching runs performed under the same conditions. The percent reduction calculations were performed according to equation 4.1.

$$\% \text{ Reduction} = \frac{[\text{ClO}_3^-]_{\text{T, Substitution}} - [\text{ClO}_3^-]_{\text{T, Substitution, [V}_2\text{O}_5]}}{[\text{ClO}_3^-]_{\text{T, Substitution}}} \times 100 \quad (4.1)$$

#### 4.1.1. The Effect of Catalyst Charge

Tables 4.2 and 4.3 show that the catalyst charge has a large impact on the residual chlorate concentration..

The catalytic bleaching reactions are believed to proceed through the vanadium cycling mechanism illustrated in Figure 2.7 (Deutsch *et al.* 1979, Rapson *et al* 1959, Marpillero 1958).

#### Interpreting Interaction Effects in Factorial Design

The effect of the interaction between two variables is calculated as follows:

$$\text{interaction effect} = \frac{Y_{++} + Y_{--}}{2} - \frac{Y_{+-} + Y_{-+}}{2}$$

$Y_{++}$  and  $Y_{--}$  are the system responses with both variables at their high, and low factor settings, respectively.

$Y_{+-}$  and  $Y_{-+}$  are the system responses with one variable at its high setting and the other at its low setting.

If the interaction effect is 0, then the effect of the two variables is additive, and no significant interaction occurs. If the interaction effect is positive, then the two variables interact synergistically to increase the value of  $Y$ ; if they interact negatively, then the variables interact to reduce the value of  $Y$ .

Variable	Factor Levels (Low/High)	Residual Chlorate (mM)	95 % confidence interval	Chlorate Eliminated (mol %)	95 % confidence interval
Main Effects					
pH (at start of bleaching)	2/4	0.018	0.017	-10.61	1.53
Temperature (°C)	70/80	-0.240		42.12	
Substitution (% eq. chlorine)	50/100	0.019		-21.40	
Catalyst Charge (wt. % on oven dry pulp)	0.001/0.010	-0.220		52.45	
Interaction Effects					
Temperature/pH	-	0.020	0.017	3.33	1.53
Substitution/pH	-	-0.019		21.40	
Catalyst/pH	-	-0.005		-3.12	
Substitution/Temperature	-	0.018		15.46	
Substitution/Catalyst	-	0.052		-10.12	
Catalyst/Temperature	-	0.040		0.09	

**Table 4.2: Results of the factorial analysis of chlorate concentration for Experimental Program 1.**

The chlorate reduction reaction shown in Figure 2.7 is clearly a function of vanadium concentration. With increased catalyst charge, the rate of reaction increases and the final chlorate concentration is reduced.

The chlorate reduction is most efficient at catalyst charges between 0.005 % and 0.01 %. Comparing Tables 4.2 and 4.3 shows that increasing the catalyst charge from 0.001 % to 0.01 % had a much larger effect than does the increase from 0.005 % to 0.015 %.

This is further illustrated in Figure 4.1, which shows that comparatively small reductions in final chlorate concentration were obtained with increases in catalyst charge beyond 0.005%.

Variable	Factor Levels (Low/High)	Residual Chlorate (mM)	95% confidence interval	Chlorate Eliminated (mol %)	95 % confidence interval
Main Effects					
Time (min.)	120/240	-0.071	0.017	36.98	1.53
Temperature (°C)	70/80	-0.025		26.02	
Substitution (% eq. Chlorine)	50/100	-0.001		-11.99	
Catalyst Charge (wt. % on o.d. pulp)	0.005/0.015	-0.015		37.82	
Interaction Effects					
Temperature/Time	-	-0.003	0.017	-3.58	1.53
Substitution/Time	-	-0.001		5.47	
Catalyst/Time	-	-0.039		-15.76	
Substitution/Temperature	-	-0.010		-3.21	
Substitution/Catalyst	-	-0.014		7.85	
Catalyst/Temperature	-	-0.010		4.91	

**Table 4.3: Results of the factorial analysis of chlorate concentration for Experimental Program 2.**

#### **4.1.2. The Effect of Temperature**

Temperature had the largest main effect on chlorate reduction of any of the variables tested.

As seen in Tables 4.2 and 4.3, temperature was an important factor at all catalyst charge levels. Increasing the temperature increased the rates of reaction in solution and resulted in lower final chlorate concentrations.

The influence of temperature is further illustrated in Figure 4.2. Increasing the temperature from 70°C to 80°C resulted in significantly lower residual chlorate concentrations at both 50% and 100% substitution.

The temperature was not increased beyond 80°C because adverse effects on pulp viscosity resulted when the temperature was increased to 85°C and 90°. The impact of the catalytic system on viscosity is discussed in detail in section 4.3.1.

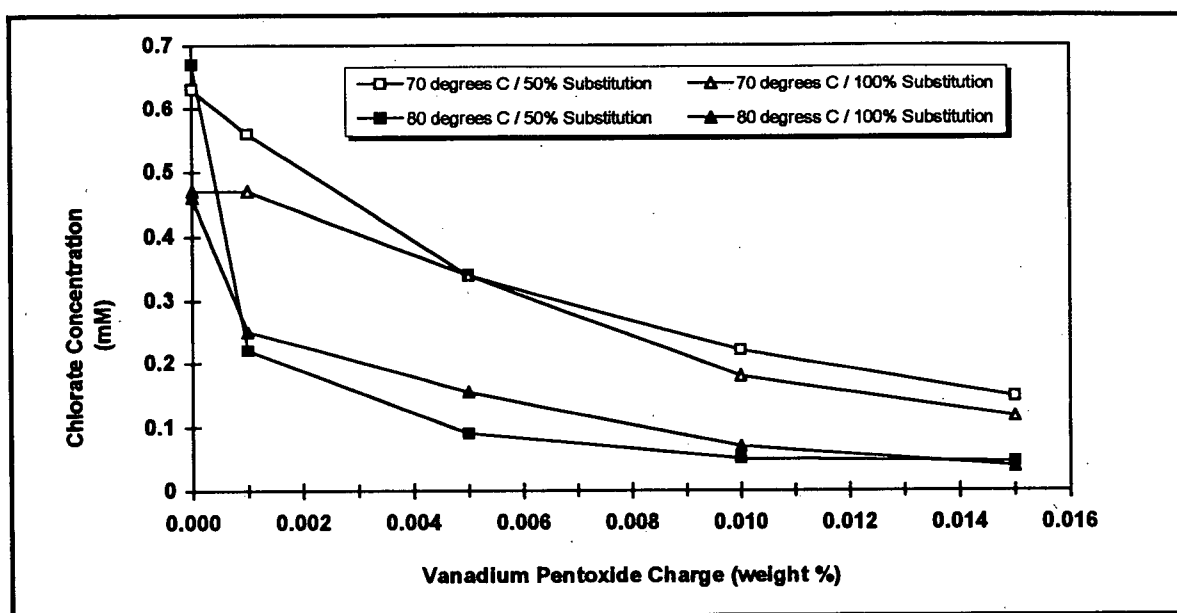
#### **4.1.3. The Effect of Reaction Time**

Table 4.2 shows that increasing the reaction time from 2 to 4 hours has a large main effect on the chlorate concentration. This agrees with the work of Deutsch *et al.* (1979), who studied vanadium pentoxide "activation" of the chlorate residual in chlorine dioxide brightening. They found that reaction times of greater than 2 to 3 hours were required for significant drops in chlorate concentration.

Since chlorate formation nears completion after 30 to 40 minutes (Ni *et al.* 1993), the rate of chlorate formation does not account for the long retention times required for the chlorate reduction reactions. It is the rates of the cycling reactions shown in Figure 2.7 that determine the overall rate of chlorate reduction. No directly applicable quantitative data concerning the rates of reaction of  $V^{+5}$  with organics or  $V^{+4}$  with chlorate were found in the literature.

#### **4.1.4. The Effect of Chlorine Dioxide Substitution**

Tables 4.2 and 4.3 show the main effects of substitution on the final chlorate concentration and the percent reduction in chlorate concentration. While the impact of substitution on final chlorate concentration was not significant, the percent reduction in chlorate concentration was a strong function of substitution. The substitution had a large effect on the percent reduction in chlorate concentration because more chlorate was formed at 50%



**Figure 4.1: Chlorate concentration as a function of catalyst charge, temperature, and substitution. (Bleaching conditions: final pH of 2.5, retention time of 240 minutes.)**

substitution than at 100% substitution in the uncatalyzed runs, while the final chlorate concentration in the catalyzed runs was nearly equal for both substitution levels.

As a result, the reductions in chlorate concentration were larger in the 50 percent substitution runs than in the 100 percent substitution runs. A detailed discussion of the impact of substitution on the final chlorate concentration and the percent reduction in chlorate concentration for the catalyzed and uncatalyzed runs is presented in sections 4.1.4.1 through 4.1.4.3.

#### 4.1.4.1. Effect on Chlorate Formation in Uncatalyzed Bleaching

The degree of substitution has a major impact on the concentration of chlorate in chlorine dioxide bleaching liquors (Ni *et al.* 1993, Reeve and Weishar 1991, Rapson and Reeve 1980).

As shown in Table 4.4, the chlorate formed in the uncatalyzed bleaching runs was not a linear function of chlorine dioxide substitution. The final chlorate concentration was a minimum at 100% substitution, increased to a peak value at 75%, and fell back to an intermediate value at 50% substitution.

Substitution	Chlorate concentration (mmol/l)	Fraction of ClO <sub>2</sub> charge as chlorate (mol %)
50	0.661	24.1
75	0.917	22.3
100	0.460	8.4

**Table 4.4: Chlorate production in the uncatalyzed bleaching runs.**

This relationship between chlorate concentration and substitution agrees with previous reports. Farr (1991) found that for simultaneous chemical addition, chlorate formation was a maximum at approximately 60% substitution; the chlorate concentration at 50% substitution was lower than at 75% substitution. These results are further supported by earlier studies which found chlorate formation to have a local maximum at 70% to 85% substitution (Reeve and Rapson 1980, Bergnor *et al.* 1987, Axegard 1987, Germgard and Karlsson 1988).

The chlorate concentration profile for the uncatalyzed bleaching runs can be explained using the mechanism proposed by Ni *et al.* 1993), in which chlorate is formed from the reaction of



chlorite and hypochlorous acid. Using this mechanism, the trends found in chlorate formation can be explained as follows:

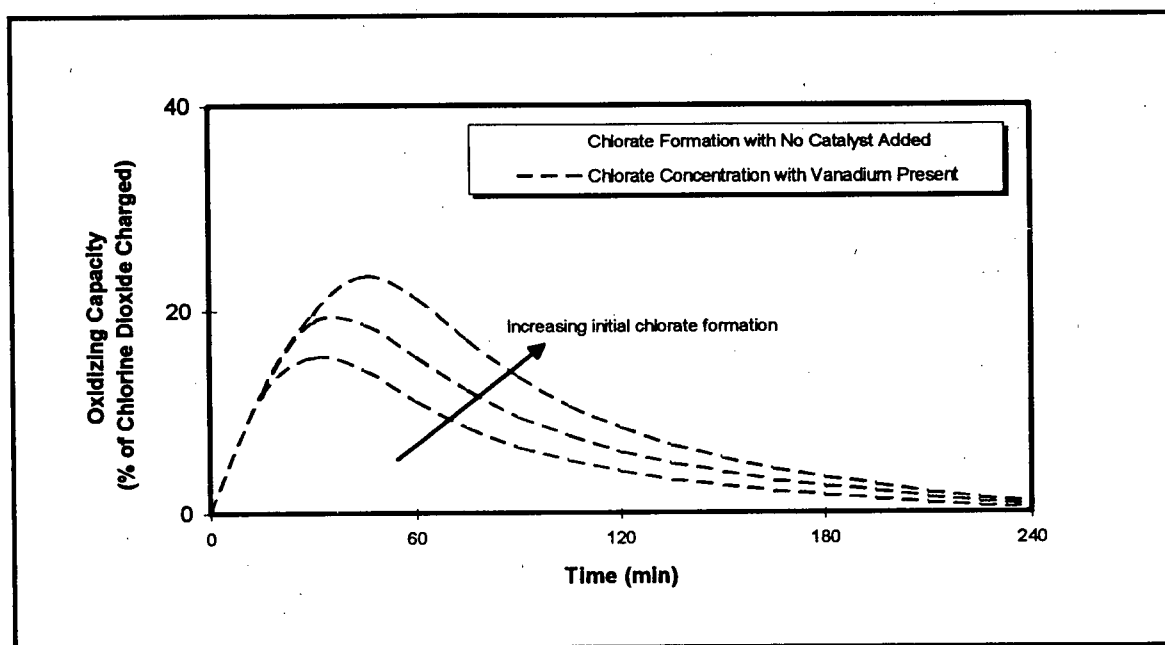
- 75% substitution: High concentrations of both hypochlorous acid and chlorite in solution results in substantial chlorate formation.
- 50% substitution: Relatively lower chlorite concentration results in less chlorate formation than at 75% substitution
- 100% substitution: Although the concentration of chlorite in solution is a maximum, there is little hypochlorous acid available for the chlorate formation reaction, and the final chlorate concentration is lower than for 50% or 75% substitution.

#### **4.1.4.2. Effect on Chlorate Concentration in the Catalyzed Runs**

The effect of substitution on the chlorate concentration found in the catalyzed system can be seen in Figure 4.1 and in Tables 4.2 and 4.3. Despite the large impact of chlorine dioxide substitution on the formation of chlorate in uncatalyzed bleaching solution, the final chlorate concentration was not strongly dependent on substitution when vanadium pentoxide was added to the bleaching liquor.

At catalyst charge levels of 0.001% and 0.005%, the main effect of substitution on final chlorate concentration was barely significant; at catalyst charges of greater than 0.005 weight percent, substitution was not a significant factor in final chlorate concentration (see Tables 4.2 and 4.3).

Figure 4.2 further illustrates that the chlorate concentration in the catalyzed bleaching runs was largely independent of the chlorine dioxide substitution. At catalyst charges of 0.01 % and greater, the chlorate concentration was approximately the same at 50% and 100% substitution.



**Figure 4.2:** An illustration of chlorate concentration profiles in catalyzed and uncatalyzed chlorine dioxide bleaching.

The small impact of substitution on the final chlorate concentration can be explained using Figure 4.2. Although the maximum chlorate concentration achieved is higher at 50% substitution than at 100% substitution, after 4 hours of reaction with the catalyst, the chlorate concentrations are approximately equal. The higher chlorate concentration achieved at 50% substitution results in a higher rate for the chlorate reduction reaction. As the reaction proceeds and the chlorate concentration drops, the rate of the reaction slows. After 4 hours, the rate of reaction and the chlorate concentration for the 50% substitution case matches that for the 100% substitution case.

#### **4.1.4.3. Impact of Substitution on the Percent Reduction of Chlorate in Catalytic Bleaching**

Although the final chlorate concentration was not strongly affected by the degree of substitution, the percent reduction in chlorate concentration was. The large effect of substitution on the percent reduction does not indicate a significant impact on the performance of the catalyst; rather, the large reductions are the result of the impact of substitution on chlorate formation. The large percent reductions in chlorate concentration were found because

- the amount of chlorate formed in the uncatalyzed runs varied with chlorine dioxide substitution, while
- the final chlorate concentration in the catalyzed runs was similar at all substitution levels

Since the percent reduction is calculated according to equation 4.1, the impact of substitution on the amount of chlorate formed had a large impact on the percent reduction of chlorate.

#### **4.1.5. The Effect of pH**

Table 4.2 shows that the impact of pH was similar to that of substitution. The effect of the starting pH of the solution on the final chlorate concentration was barely significant, yet pH had a large impact on percent reduction in the chlorate concentration.

The pH in the delignification stage is known to have a large impact on chlorate formation (Reeve and Weishar 1992, Wartiovaara 1985). Lowering the pH results in less chlorate formation during chlorine dioxide bleaching. Chlorate is formed from the reaction of

chlorite and hypochlorous acid (*Ni et al.* 1993). As shown in Figure 2.5, decreasing the pH shifts the chlorine/hypochlorous acid equilibrium towards elemental chlorine, and less hypochlorous acid is available to react with chlorite.

Substitution and pH both have large impacts on chlorate formation in the uncatalyzed bleaching runs, and little impact on the final chlorate concentration for the catalyzed bleaching runs. As a result, the discussion of the effect of starting pH on the final chlorate concentration and the percent reduction in the catalytic system is analogous to the discussion presented for substitution.

#### **4.2. The Recovery of the Bleaching Power Lost to Chlorate**

One of the primary objectives of the research was to investigate the impact of vanadium pentoxide addition on bleaching efficiency in the delignification stage. According to the reaction mechanism shown in Figure 2.7, adding vanadium pentoxide to the (D+C) stage should recapture the bleaching power lost as chlorate.

The response of the bleaching efficiency to catalyst addition was measured through the (D+C)E brightness and kappa number. Although the impact on brightness was significant, the kappa number was not significantly affected by adding vanadium to the (D+C) stage.

Since the brightness of the pulp is increased, the vanadium reactions must result in the oxidation of the chromophores in the lignin. The lack of impact on the kappa number of the pulp indicates that the vanadium oxidation reactions tend not to contribute to the dissolution of the lignin during vanadium catalyzed bleaching.

The response of the kappa number and the brightness to vanadium pentoxide addition to the delignification stage is discussed in the following sections.

#### **4.2.1. The Kappa Number Response**

The factorial analysis summarized in Table 4.5 shows that at 95% confidence, there was no significant decrease in the (D+C)E kappa number with vanadium pentoxide addition. Of the factors studied, substitution was the only parameter which significantly changed the kappa number.

It is well known that the delignification efficiency is a function of the degree of substitution and the mode of addition of chlorine/chlorine dioxide mixtures (Hatton 1967, Hatton 1966, Munro *et al.* 1990, Pryke 1992, Macas and Evans 1994, Reeve and Weishar 1991, Solomon *et al.* 1993). In this study, the 100% substitution and the 50% substitution (D+C)E uncatalyzed bleaching sequences yielded kappa numbers of 5.6 and 6.2, respectively.

Usually, delignification is found to be more efficient at 50% substitution than at 100% substitution. The disagreement found in the current work is attributed to the variable nature of pulp reactions. Changing pulp sources and reaction conditions has a large impact on the delignification efficiency and, therefore, the final kappa number of the bleached pulp.

Variable	Kappa number (ml)	Brightness (ISO)	Brightness Gain (ISO)
95% Confidence Interval	0.54	0.83	0.83
Main Effects			
Time	0.01	-0.42	-0.42
Temperature	-0.09	-0.50	0.90
Substitution	-1.01	2.89	-0.48
Catalyst Concentration	0.04	1.17	1.17
Interaction Effects			
Temperature/Time	0.21	-0.75	-0.75
Substitution/Time	-0.16	-0.42	-0.42
Catalyst/Time	-0.11	0.11	0.82
Substitution/Temperature	0.09	0.41	-0.82
Substitution/Catalyst	0.26	-0.26	0.17
Catalyst/Temperature	-0.01	0.59	0.59

**Table 4.5: The factorial analysis of the (D+C)E kappa number and brightness responses.**

Since oxygen pre-bleaching removes a large fraction of the initial lignin content of the pulp, we suspected that the impact of the vanadium oxidations on kappa number was masked by using the oxygen delignified pulp. The hypothesis was that by removing the easily oxidized lignin through oxygen pre-bleaching, the potential for catalytic delignification was masked.

To examine the impact of oxygen pre-bleaching on the kappa number of "activated" chlorate bleached pulps, several runs from Table 4.4 were repeated using unbleached kraft pulp. As found for the oxygen pre-bleached pulp runs, the "activation" of the chlorate residual in the delignification of unbleached kraft pulp did not have a significant impact on the kappa number of the bleached pulp.

There is no obvious explanation for the lack of kappa number reduction with vanadium pentoxide catalyzed bleaching. Since no information regarding the detailed mechanism of the reaction between pentavalent vanadium and lignin is available, it must be assumed that the oxidation reactions that occur do not promote lignin dissolution during chlorine dioxide bleaching or the subsequent caustic extraction.

#### **4.2.2. The Brightness Response**

Contrary to the response of kappa number, the bleached pulp brightness did provide evidence of chlorate "activation" when vanadium was added to the chlorination stage. Table 4.5 shows that at 95% confidence, both catalyst charge and substitution have significant main effects on the brightness of the bleached pulp.

The brightness gains shown in Table 4.5 can be correlated to increased activity of the vanadium catalyst. Average brightness gains, compared to uncatalyzed bleaching runs at the same temperature, of approximately 1 percent were found for increases in temperature or catalyst charge. Since increases in temperature and catalyst charge were found to increase catalyst activity (Section 4.1), the brightness gains are attributed to "activation" of the chlorate residual.

##### **4.2.2.1. Brightness from Catalyzed and Uncatalyzed Bleaching Runs**

In the previous section, we found brightness gains with catalyst addition when compared to uncatalyzed bleaching runs at the same temperature. When compared to bleaching runs at 40°C, however, there are no brightness gains associated with the "activated" chlorate system.

Figure 4.3 shows that the brightness of the uncatalyzed bleaching runs decreased as temperature was increased. When chlorine dioxide bleaching sequences are operated at greater than 70°C, the oxidant charge may be completely consumed, and brightness losses may occur (Rapson and Strumila 1979). Since we used a relatively low charge factor of 0.15, long bleaching runs, and high temperatures, there was no residual oxidant charge remaining at the end of the bleach<sup>a</sup>. The result was diminished brightness in the uncatalyzed bleaching runs as the temperature was increased.

Figure 4.3 also compares the brightness attained with catalyzed bleaching runs at 70°C and 80°C with uncatalyzed bleaching runs at 40°C, 70°C, and 80°C. Although the addition of catalyst results in higher brightness at 70°C and 80°C, the brightness gains do not compensate for the losses in brightness associated with increasing the temperature from 40°C to greater than 70°C.

In summary, higher final brightnesses were obtained for uncatalyzed bleaching runs at lower temperature than for the catalyzed bleaching runs and vanadium pentoxide addition is ineffective at recovering the bleaching power lost as chlorate in the delignification stage.

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<sup>a</sup>Ni *et al.* showed that at 45°C and a charge factor of 0.22, there is no residual oxidant charge after 120 minutes. Given the increase in the rate of reaction with an increase in temperature from 45°C to 70°C or 80°C, combined with the lower charge factor of 0.15 used in this study, the oxidant charge is guaranteed to be fully consumed.



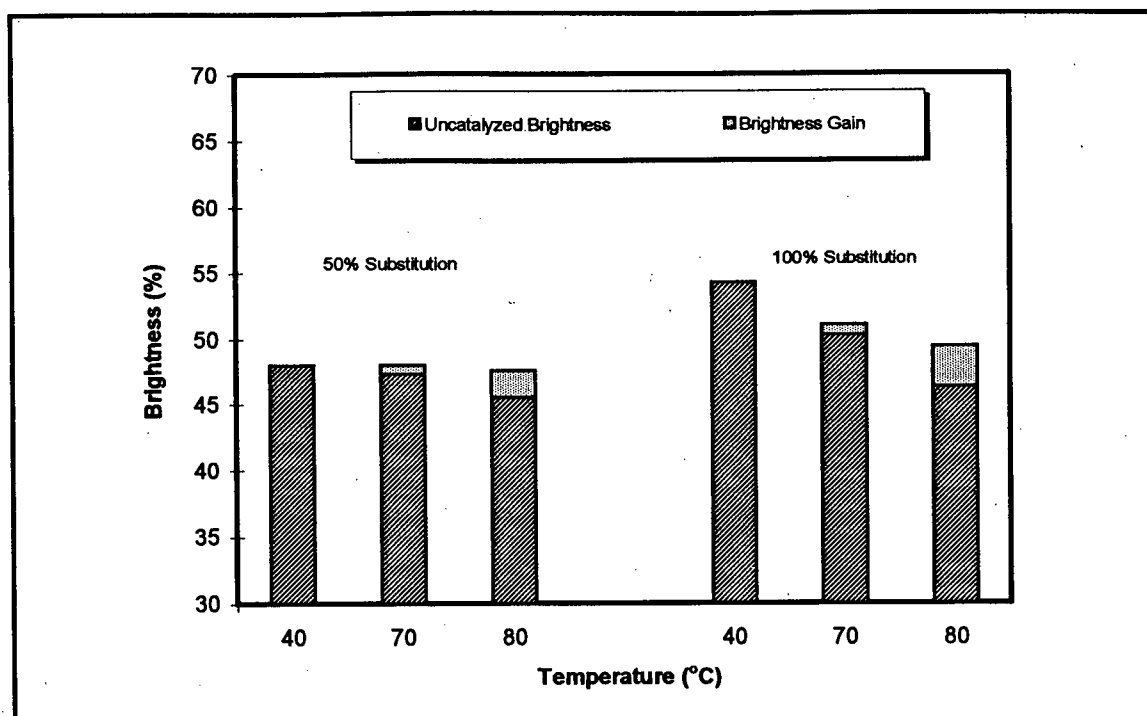


Figure 4.3: Brightness as a function of temperature and substitution.

#### 4.3. The Impact of the Catalytic Bleaching on Pulp Properties

To gain some insight into the impact of vanadium addition on the bleached pulp quality, testing of the physical properties of the catalyzed and uncatalyzed bleached pulp was performed as part of Experimental Program 2. The factorial analysis of the viscosity and the strength property responses is presented in Tables 4.6 through 4.8.

A discussion of the impact of chlorate "activation" on bleached pulp properties is presented in the following sections.

### **4.3.1. Pulp Viscosity**

Table 4.6 shows the results of the factorial analysis of the pulp viscosity responses to time, temperature, substitution, and catalyst charge. All of the main effects and most of the interaction effects were significant. Increases in time, temperature, and catalyst charge tended to reduce the viscosity. The viscosity was lower for the 50% runs than for the 100% runs.

A discussion of the impact of each of the factor variables on the bleached pulp viscosity is presented in sections 4.3.1.1 through 4.3.1.3.

#### **4.3.1.1. The Effect of Chlorine Dioxide Substitution**

Of all the variables tested, the degree of substitution had the largest impact on the final pulp viscosity.

Substitution was expected to have a large effect on the bleached pulp viscosity because of the complex relationship that exists between the chlorine charge in the first stage and the viscosity of the pulp produced (Macas and Evans 1994). It has long been known that the addition of chlorine dioxide to the chlorination stage offers viscosity protection results in higher viscosity for chlorination stage pulp (Jack and Feller 1967, Hatton 1967, Hatton *et al.* 1966). Mill reports also show that increased substitution, even at greater than 50% substitution, can result in higher viscosities (Pryke *et al.* 1993). Therefore, the present findings of lower viscosity at 50% substitution than at 100% substitution are consistent with both laboratory reports and mill scale findings.

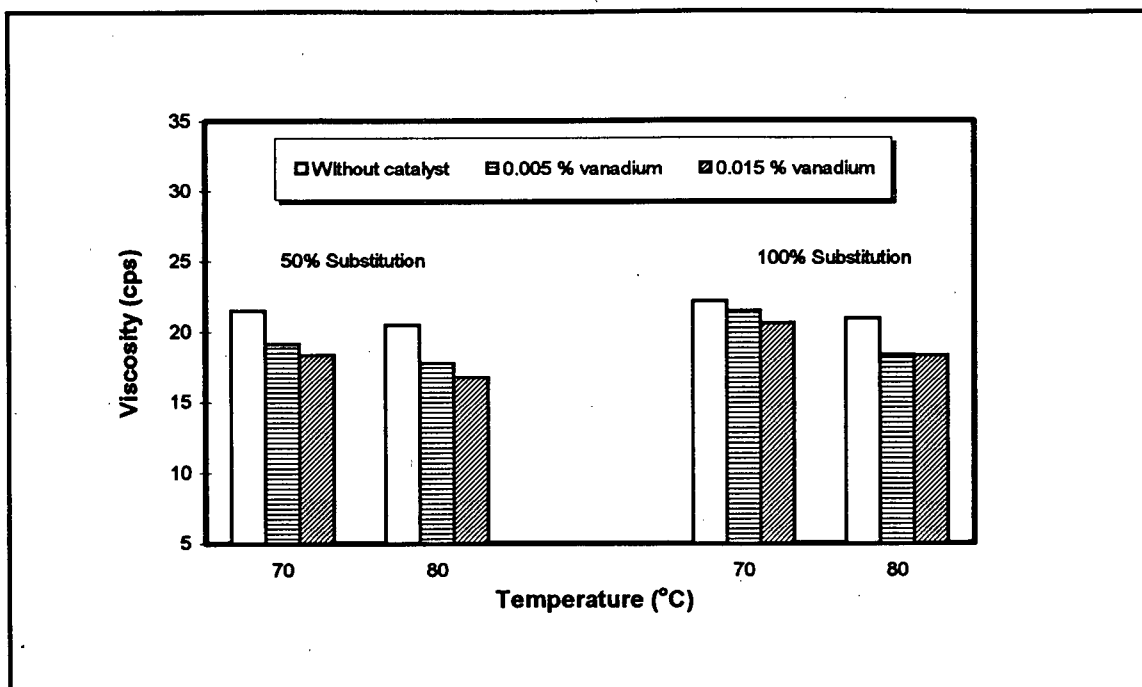
Variable	Viscosity (cps)	Viscosity Loss (cps)
95% Confidence Interval	0.20	0.2
Main Effects		
Time	-1.40	1.40
Temperature	-1.87	0.75
Substitution	2.23	-1.70
Catalyst Concentration	-0.25	0.25
Interaction Effects		
Temperature/Time	-0.24	0.24
Substitution/Time	-0.54	0.54
Catalyst/Time	-0.40	0.40
Substitution/Temperature	-0.43	0.34
Substitution/Catalyst	0.18	-0.18
Catalyst/Temperature	0.11	-0.11

**Table 4.6: The factorial analysis of the (D+C)E viscosity response.**

#### **4.3.1.2. The Effect of Catalyst Charge**

According to the factorial analysis, increasing the catalyst charge from 0.005 to 0.015 weight percent had only a small impact on the pulp viscosity.

However, the effects calculated in the factorial analysis may be misleading. As shown in Figure 4.1, increases in catalyst charge beyond 0.005 weight percent on oven dry pulp had a modest impact on chlorate elimination and did not seriously increase the catalyst activity. Since the viscosity measurements were performed on the runs operated on the flat section of the catalyst activity curve, the impact of the catalyst on the final viscosity of the pulp was not clearly shown in this catalyst charge range.



**Figure 4.4: The impact of vanadium addition on viscosity.**

Although not clearly shown in the factorial results, the vanadium oxidation reactions did have a large impact on the final viscosity of the bleached pulp. As illustrated in Figure 4.4, the pulp viscosity dropped with increases in temperature and catalyst charge, and with lower chlorine dioxide substitution. Since more vanadium oxidations occur at higher temperatures, higher catalyst charges, and at lower substitution (Section 4.1), it is evident that the viscosity loss of the pulp is directly related to the catalyst activity.

The viscosity losses associated with the catalyst activity are a result of the mechanism of vanadium pentoxide oxidations. Oxidation reactions involving pentavalent vanadium in aqueous solutions are known to proceed via free radical mechanisms (Littler and Waters, 1959). Free radical oxidations are non selective and can result in both cleavage of cellulosic chains, and lignin oxidations. The cellulose chain cleavage results in lower pulp viscosity.

#### **4.3.1.3. The Effects of Temperature and Time**

Since the catalytic bleaching operation must be conducted at low final pH values and at elevated temperature for effective catalyst action, significant losses in viscosity due to acid hydrolysis occurred (Grace *et al.* 1988).

Since the rate of acid hydrolysis increases with temperature, the viscosity losses were greater at 80°C than at 70°C, and the main effect of temperature on viscosity was large.

The large main effect of time on viscosity was a result of more extensive acid hydrolysis as the reaction time was increased.

#### **4.3.2. The Response of the Physical Properties**

Physical testing of the bleached pulp was performed to investigate the impact of the viscosity losses on the strength properties of the pulp.

The physical testing performed included the tensile index, breaking length, tear index, tear strength, burst index, burst strength, zero span index, bulk, and opacity.

As seen in Table 4.7, none of the main effects of substitution, time, and catalyst charge were significant for the runs performed at 80°C.

Parameter	Retention time	Substitution	Catalyst charge	95 % confidence interval
Tensile Index (N·m/g)	-1.29	0.17	0.38	3.28
Breaking length (km)	-0.13	0.02	0.04	0.33
Tear Index (mN·m <sup>2</sup> /g)	0.39	-0.39	-0.38	0.48
Tear strength (mN)	23.70	-23.38	-22.92	29.10
Burst Index (kPa·m <sup>2</sup> /g)	0.03	-0.07	-0.09	0.51
Burst strength (kPa)	-1.79	-0.59	-1.09	5.31
Zero Span Index (km)	-0.51	0.30	-0.25	1.03
Bulk (cm <sup>3</sup> /g)	-0.03	-0.05	-0.03	0.32
Opacity (ISO)	-0.77	-0.06	-0.06	2.59

**Table 4.7: Factorial analysis of the physical testing results for the runs at 80°C**

Furthermore, Table 4.8 shows that no significant difference was found in the strength properties of pulp bleached with and without catalyst. The factorial analysis included the effects of catalyst charge, substitution, and temperature on pulp strength. The bleached pulps used in the analysis were from uncatalyzed runs at 40°C and runs with 0.015 weight percent catalyst charge at 80°C. These pulps represent the lowest and highest degrees of cellulose degradation found in the study; the viscosities of the catalyzed and uncatalyzed bleaching run pulps were, respectively, 18.29 and 23.75, for the 100% substitution case and 16.77 and 22.21, for the 50 % substitution case.

Despite viscosity drops on the order of 5 points, to a minimum viscosity of 16.8, there was not a significant change the physical properties of the pulp. These results are supported by recent investigations of the impact of TCF and ECF bleaching sequences on pulp strength and optical properties which show that at viscosity values as low as 13 to 14 cps, the pulp quality is not adversely affected (Gottlieb *et al.*, 1993, Kappel, Brauer and Kittel 1993, Mokfienski 1994, and Francis *et al.*, 1994).

Parameter		Temperature	Substitution	Catalyst charge	95% confidence interval
Tensile Index	(N·m/g)	-1.44	1.62	-1.44	4.64
Breaking length	(km)	-0.15	0.16	-0.15	0.48
Tear Index	(mN·m <sup>2</sup> /g)	-0.19	0.23	-0.19	0.69
Tear strength	(mN)	-11.25	13.64	-11.25	41.16
Burst Index	(kPa·m <sup>2</sup> /g)	-0.24	-0.06	-0.24	0.72
Burst strength	(kPa)	-1.38	4.25	-1.38	7.51
Zero Span Index	(km)	-1.14	0.56	-1.14	1.46
Bulk	(cm <sup>3</sup> /g)	-0.09	0.04	-0.09	0.46
Opacity	(ISO)	1.98	-2.02	1.98	3.66

**Table 4.8: A comparison of the physical testing results for the 40°C uncatalyzed runs and the 80°C runs with a 0.015 weight percent catalyst charge.**

Therefore, although the "activation" of the chlorate residual does result in substantial viscosity losses, these losses are not manifested as losses in pulp strength or optical properties.

#### **4.4. Potential Applications for Vanadium in the Delignification Stage**

Although the addition of vanadium pentoxide to the first stage did not result in significant recovery of the bleaching power of chlorate, vanadium addition does have potential for reducing the chlorate concentration in the effluent from the first stage.

Figures 4.5 and 4.6 illustrate two conceptual operating flowcharts using vanadium pentoxide to reduce the chlorate discharges from the first stage.

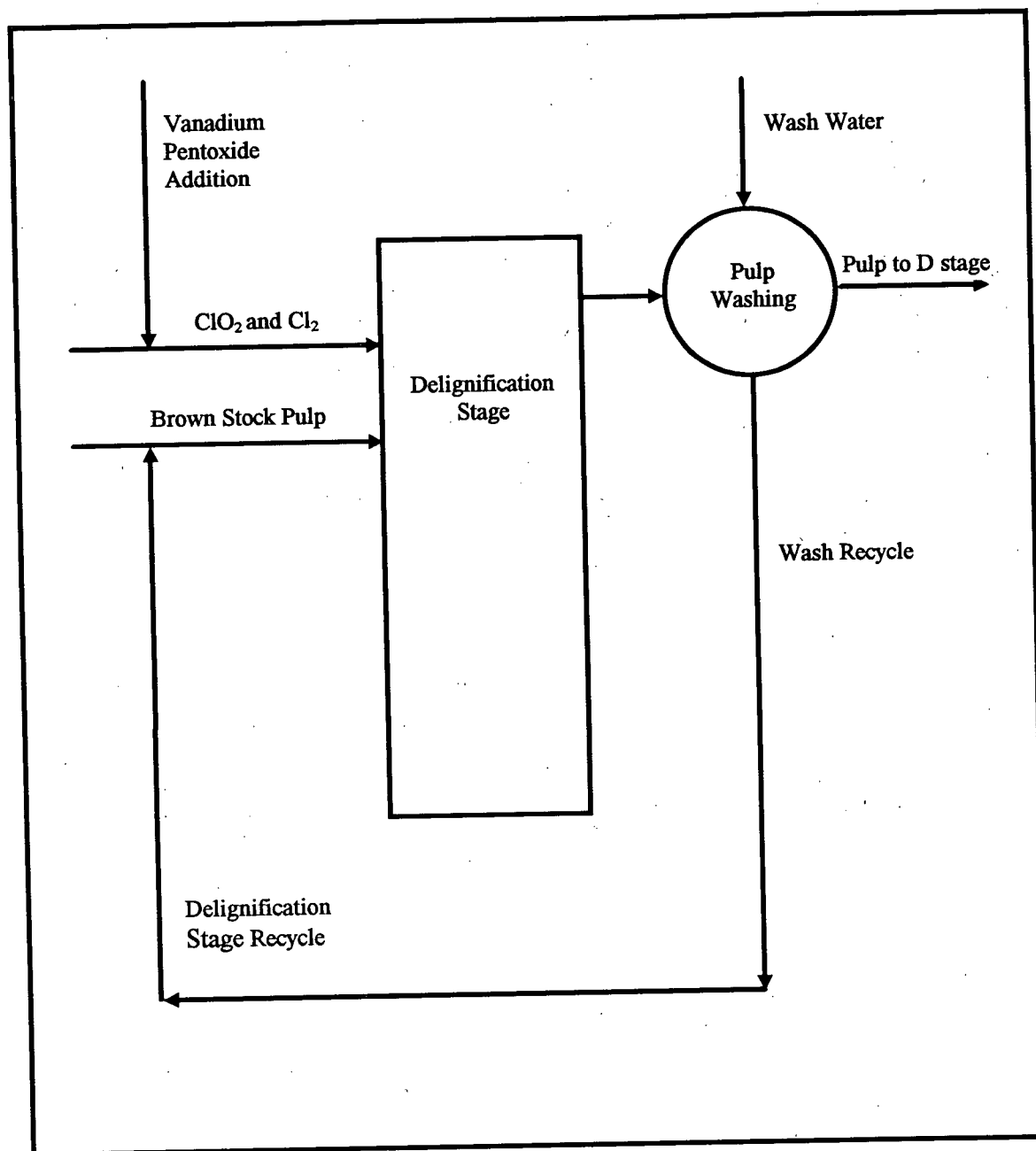
Figure 4.5, illustrates the standard operation of the chlorination stage with vanadium pentoxide added to the bleaching chemicals. A significant fraction of the chlorination stage effluent is recycled. This reduces the required vanadium charge for chlorate reduction, and minimizes the vanadium content of the bleaching stage effluent. Based on the results of this

study, reductions in chlorate concentration of up to 95% would be expected with this system.

Figure 4.6, illustrates a potential variation on the conventional chlorination stage operation, in which a vanadium stage is added to the recycle. In this scheme the vanadium could be used as an immobilized catalyst structure, perhaps as a plate or as pellets, to catalyze the reduction of the chlorate in the recycle. This would eliminate the entrainment of vanadium in bleach plant effluent. And, chlorate reduction would be accomplished without the attendant loss in pulp viscosity.

The potential for this reaction scheme to reduce the chlorate concentration in the delignification stage should be investigated.





**Figure 4.5: Conceptual flow sheet for the chlorination stage operated with vanadium pentoxide addition.**

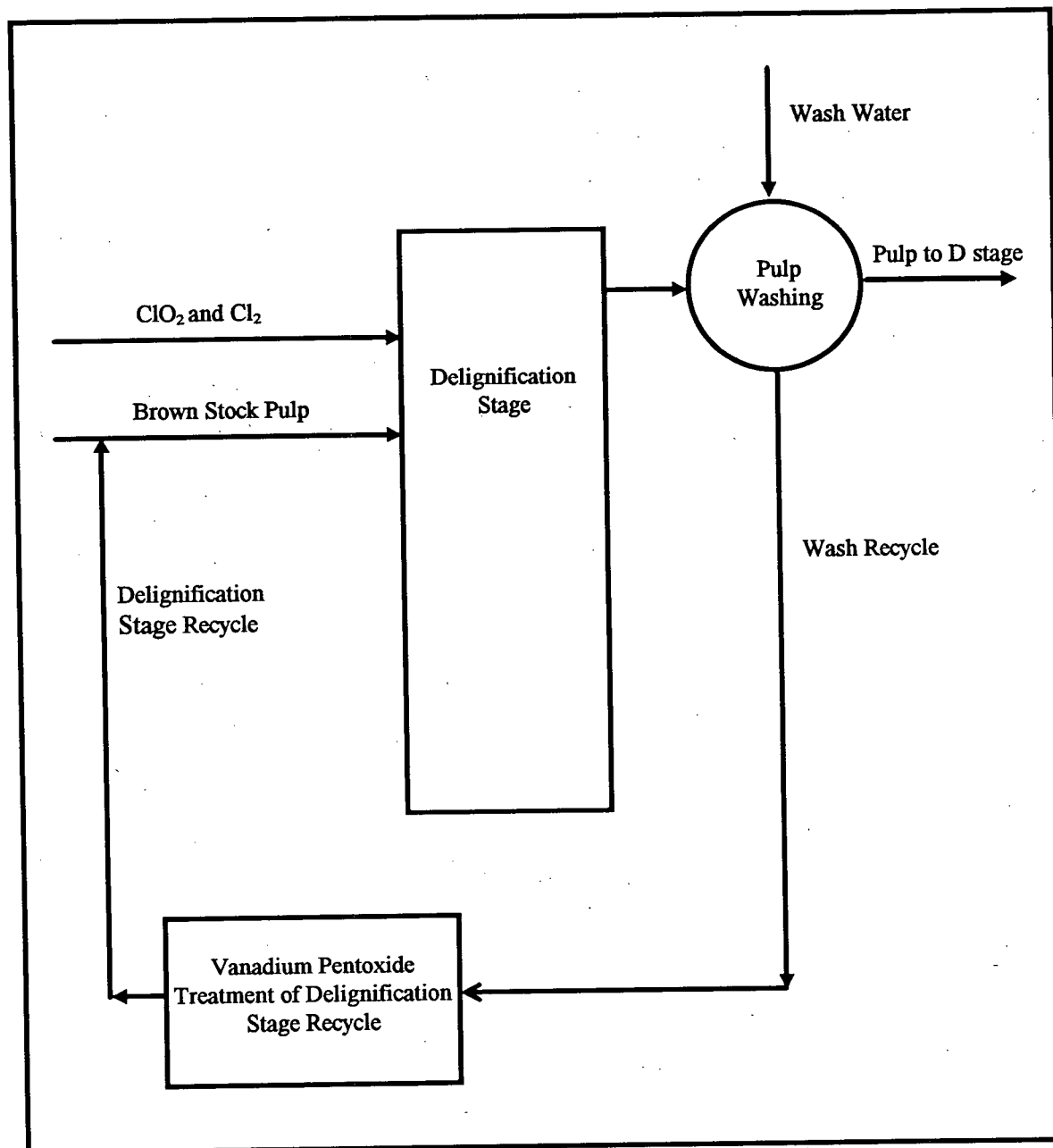


Figure 4.6: Conceptual flow sheet for the vanadium treatment of the chlorination stage recycle.

## 5. CONCLUSIONS

1. The addition of vanadium pentoxide to the chlorination stage operated at high chlorine dioxide substitution can result in reductions of greater than 90% in the final chlorate concentration.
2. Temperature has a large impact on the activity of the catalyst. Temperatures of greater than 70°C are required for "activation" of the chlorate residual with chlorine dioxide. The activity of the catalyst increases dramatically with temperature; however, the serious viscosity losses are incurred at temperatures above 80°C.
3. Retention times of greater than 2 hours are required for significant reductions in the final chlorate concentration. Retention times of approximately 4 hours are required for very low final chlorate concentrations.
4. The effect of the degree of chlorine dioxide substitution on the final chlorate concentration was barely significant for the catalyzed bleaching runs.
5. At pH values of less than 3, the final chlorate concentration was independent of pH.
6. Increases in catalyst charge beyond 0.005 weight percent did not substantially increase the activity of the catalyst for chlorate reduction.
7. The optimum conditions for vanadium pentoxide catalysis in the chlorination stage are temperature of 80°C, reaction time of 4 hours, and a catalyst charge between 0.005 and 0.01 weight percent on oven dry pulp.

8. The activity of the catalyst resulted in serious viscosity losses. The initial viscosities for the uncatalyzed bleaching runs at 50% and 100% chlorine dioxide substitution cases were 21 and 23, respectively. The catalyzed chlorination stage produced pulp with viscosity as low as 16 cps.
9. Despite significant losses in viscosity, the physical properties of the pulp produced using the catalytic system were not significantly different from those of pulp bleached using conventional chlorination.
10. The addition of vanadium pentoxide to the chlorination stage did not result in substantial gains in bleaching power. When compared to uncatalyzed bleaching runs at the same temperature, the addition of vanadium pentoxide resulted in brightness gains of approximately 1 percent; however, the final brightness of the catalytically bleached pulps was lower than pulps bleached without catalyst at 40°C. There was no significant decrease in Kappa number associated with vanadium pentoxide addition.
11. Although vanadium pentoxide catalysis of chlorine dioxide delignification is not a reasonable strategy for increasing the bleaching effectiveness, it does offer a potential method for reducing the chlorate concentration in the chlorination stage effluent.

## 6. RECOMMENDATIONS

1. More assessment of the problem of the chlorate production in North American pulp mills is required. Outside of Sweden, little attention has been given to the problem of chlorate formation. Because the bleach plants in North American pulp mills are being operated with ever increasing levels of chlorine dioxide substitution in the delignification stage, the problem of chlorate formation in the North American context must be addressed.
2. A search for other potential catalysts capable of "activating" the chlorate residual with more specific and effective oxidation of lignin should be carried out. Organic catalysts are of particular interest. An organic catalyst could be used in closed cycle mill operations where the solids contained in the bleach plant effluent are burned. Unlike vanadium pentoxide, an organic catalyst would form carbonaceous combustion products.
3. There is potential for vanadium pentoxide to be used to treat the chlorate contained in the chlorination stage recycle. The catalyst could be used in a solid form such as plates or immobilized pellets to eliminate the entraining of vanadium in the effluent stream. Conceptually, the chlorination stage recycle would contact the catalyst and the chlorate would be reduced to chloride. The final chlorate concentration could potentially be reduced to very low levels without releasing vanadium to the environment. The potential for this type of treatment for chlorate elimination should be investigated further.

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## **APPENDIX A**

### **THE DETAILED CATALYTIC BLEACHING PROCEDURE**

## CATALYTIC BLEACHING PROCEDURE

The bleaching runs were performed using the bag bleaching technique. The following steps were followed for each bleaching run:

1. The concentration of the chlorine and chlorine dioxide solutions was determined using the iodometric determination technique described in Section 3.2. From this determination, the volume of chlorine and chlorine dioxide to be used in the bleaching run was computed.
2. The pulp was weighed out to the nearest 0.01g and added to the water required to bring the final bleaching solution to 3.5% consistency.
3. The required volume of catalyst was charged to the pulp and water mixture.
4. While mixing the pulp suspension thoroughly with a mechanical stirrer, the pH of the solution was adjusted to the desired level using concentrated hydrochloric acid.
5. The pulp suspension was then poured into the polyethylene bag. A clamp was placed across the bag, just above the level of the pulp suspension. The top of the bag was sealed with multiple heat treatments.
6. The chlorine and chlorine dioxide solutions were then charged via syringe from stoppered glass neck flasks to the empty upper section of the bag. The punctures in the bag were isolated from the main bag section using multiple heat seals.
7. The clamp was removed from the bag and the water was squeezed carefully from the pulp suspension into the oxidant solution and mixed.
8. Timing was started when the diluted oxidant charge was added and kneaded thoroughly to mix with the pulp in the bag. The bag was then immersed in a constant temperature bath.
9. The pulp suspension was thoroughly mixed after 10 minutes and at 20 minute intervals thereafter for the first hour. The mixing was performed at

30 minute intervals following the first hour for the duration of the bleaching run.

10. The bags were removed from the constant temperature bath and rapidly cooled in a cold water bath. The pulp was then filtered from the bleaching liquor and washed with water using an aspirated Buchner funnel apparatus.

## **APPENDIX B**

### **THE CHLORINE DIOXIDE GENERATION PROCEDURE**



## THE CHLORINE DIOXIDE GENERATION PROCEDURE

The apparatus used for the production of the chlorine dioxide solution is illustrated in Figure B.1.

The chlorine dioxide solution was prepared by acidifying sodium chlorite. 50 g of sodium chlorite was added to flask number 1. 300 and 100 millilitres, respectively, of 200 g/l sodium chlorite solution was added to flasks 2 and 3. Flask number 4 was filled with 1 litre of deionized water and cooled in an ice bath. The aspirator attached to the system was then turned on.

The reaction was initiated by dropping 10 N sulfuric acid from the dropping funnel, apparatus number 7, to the concentrated chlorite solution in flask number 1. The first 5 millilitres of 10 N sulfuric acid were added very slowly and the reaction was monitored carefully. A vigorous reaction would start immediately and vent number 6 was left open to ensure adequate air flow through the generating flask. While maintaining a controlled reaction, more sulfuric acid was added until a total of 500 ml of 10 N sulfuric acid was added to the system.

Once the addition was complete, vent number 6 was closed and the chlorine dioxide/acid solution in flask 1 was stripped with air until the gaseous green colour of the chlorine dioxide entering flask number 4 was nearly gone. The result was a chlorine dioxide solution of approximately 4 to 5 g/l with an undetectable amount of chlorine in solution.

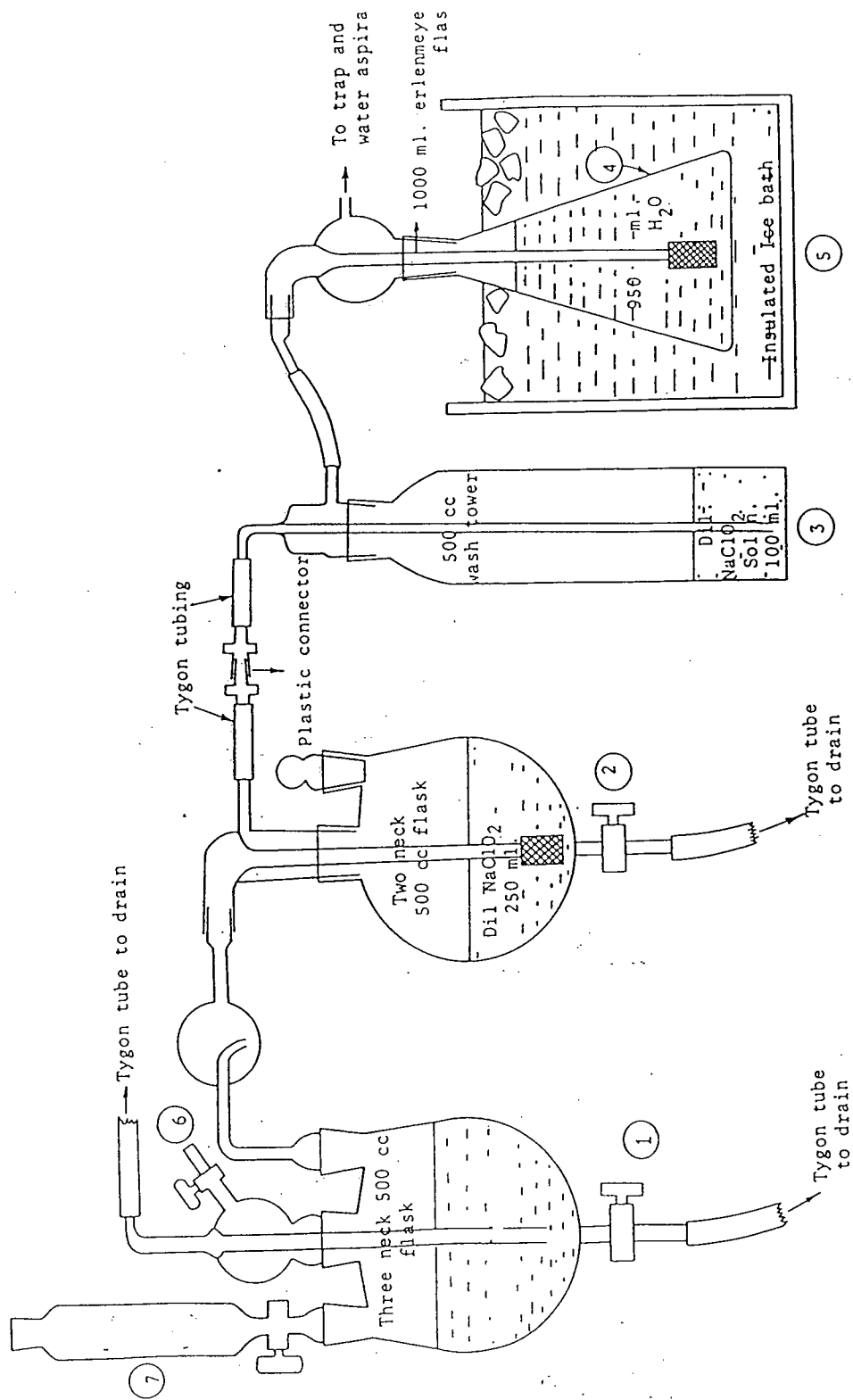


Figure B.1: The chlorine dioxide generation apparatus.

## **APPENDIX C**

### **DESIGN AND ANALYSIS OF INDUSTRIAL EXPERIMENTS**

**(MURPHY, 1977)**

# Design and analysis of industrial experiments

The basic principles and practical aspects of experimental design are presented here for the various stages of an R & D investigation. Statistical data analysis techniques that can be applied with the designs are also provided.

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□ Statistical design of experiments is a proven technique that continues to show increasing use in the chemical process industries (CPI). As the R & D function comes under increasing pressure to produce fast, accurate results, more chemists and chemical engineers are recognizing the assistance that experimental design can provide.

What are the benefits of this technique? Perhaps the most important one is that it can give more information per experiment than unplanned approaches. Chemists and chemical engineers who practice statistical design say that it reduces their lead time and improves their efficiency, particularly when many variables are of potential importance.

A second benefit is an organized approach toward the collection and analysis of information. Very often, the conclusions from a statistically designed experiment are evident without extensive statistical analysis. A haphazard approach, on the other hand, can yield results that are difficult to extract, even by a knowledgeable statistician.

Another advantage is an assessment of information reliability in the light of experimental and analytical variation. This self-criticism of the results, when presented in a report, lends more credibility to the experimenter's conclusions, since nearly everyone reading the report will apply some of his own judgment of the reliability of the data.

A fourth benefit is the capability to see interactions among experimental variables, leading to more-reliable predictions of the response data in areas not directly covered by experimentation. Many investigators mistakenly persist in the belief that experimental variables have an additive effect which is often not borne out in chemical practice.

## Stages of investigation

Chemical investigations pass through a well-defined series of stages, whether they are bench studies, pilot-plant programs, plant trials or plant startups. Each stage presents its own objectives and difficulties, as follows:

*Familiarization*—In this stage the investigator is be-

coming acquainted with a system, perhaps trying to duplicate patent results or experiments from a prior study, or learning to operate new equipment. Statistical design is generally not very fruitful here, since most experiments are conducted on an intuitive basis.

*Variable screening*—After the goals of the investigation are better defined, the next step is to reduce the large number of potential variables to a few effective ones. Unfortunately, the intuitive approach of the previous stage is often carried along into this one, investigating variables one or two at a time, and ending up with a large mass of disorganized data. Statistical design is very useful and productive at this stage, and imposes a considerable amount of discipline on the experiment.

*Optimization*—In progressing to the optimization stage, the number of variables has been reduced to an effective few, but it is necessary to find their best settings in order to make the best product at the lowest cost, effluent, or energy. Statistical design can help to arrive quickly and efficiently at the optimum, and it can provide a mechanism for evaluating tradeoffs among product properties, costs, and other important attributes.

*Mechanistic studies*—If the process or product looks technically promising, and commercial signs are favorable, then a theoretical or mechanistic model may be necessary to aid in plant design. Statistical experimental design can assist in choosing among candidate theoretical models and in estimating the system parameters most precisely. Box and Lucas [4] describe a useful procedure for selection of designs in this phase.

The purpose of this article is to introduce the experimenter to the many practical aspects of experimental design, and to indicate where statistical methods can assist in arriving at meaningful conclusions from experimental data. The following section covers the basic principles of statistical design for the important variable-screening and optimization stages of the investigation. The final section gives some statistical-data-analysis techniques that can be applied with the designs.

## Designing experiments

The many elements to consider in an experimental design are shown in Table I. We will define and discuss

these elements, showing how their interrelationships influence the resulting design, and how the design relates to a particular stage of the experimental program; a simple example will be used to illustrate.

Since the word "experiment" may be ambiguous, this word, as well as other terms used in a statistical design, will be defined. An experimental run, (here shortened to run) is simply a single experiment. A group of runs, directed toward meeting some objective, will be termed an experimental design, or simply a design.

The anatomy of a run is pictured in Fig. 1. The outcome of a run is a response or observation made on a physical experimental unit. The value of a response for any given run will vary depending on the settings of one or more experimental variables, or factors, which are under the direct control of the experimenter. In a plastics-molding experiment, for example, the experimental unit may be a molded-plastic specimen, the factors may be molding conditions, such as temperature, pressure and dwell time, and one response might be tensile strength.

Sometimes the experimental unit may not be well defined. In a chemical reaction, the experimental unit might be thought of as the apparatus, the materials and the technician.

Unfortunately for experimenters, this picture of an experimental run also includes the many uncontrolled (and even unknown) variables that also influence response. These variables give rise to both systematic and random variations that tend to mask the true effects of the factors on the response. Examples of systematic effects are ambient conditions and differences in equipment, starting materials and technique. Some random variations may be caused by weighing errors, material transfers, and instrument readings. A good experimental design must consider the impact of such variability on the ability to draw sound conclusions and meet experimental objectives.

## Response variables

Response variables are the data from an experimental run. In most investigations there are several responses, some of which may be conflicting. This tendency may lead to eventual compromises in arriving at the final decision.

It is good practice to have well-defined procedures for performing the experiment and measuring the response. Too often, the experimenter may be unfamiliar with the details of the analytical method or physical test. If so, a discussion with the person responsible for this work would be in order. If only a portion of the entire experimental unit is used for testing, an appropriate sampling procedure must also be written. This is particularly important if the experimental unit is nonhomogeneous, such as in the case of a slurry or a mixture of solids.

Responses can be classified according to measurement scale into three main types: quantitative, qualitative, or quantal. The quantitative or continuous response, such as yield, color or tensile strength, is the easiest to work with in subsequent analysis. More difficult to handle, but frequently encountered, are qualitative or categorical responses like luster, lumpiness or odor. These are easier to evaluate if a 5-10-value nu-

## Elements of experimental design

Table I

1. Statement of problem
2. List of response variables
3. List of factor variables
4. Mathematical model
5. Choice of factor levels
6. Size of design
7. Order of experimentation
8. Recording of data

merical scale can be constructed, converting the response to a semiquantitative variable. For example:

0	Equal to standard
$\pm 1$	Slight difference from standard
$\pm 2$	Moderate difference from standard
$\pm 3$	Extreme difference from standard

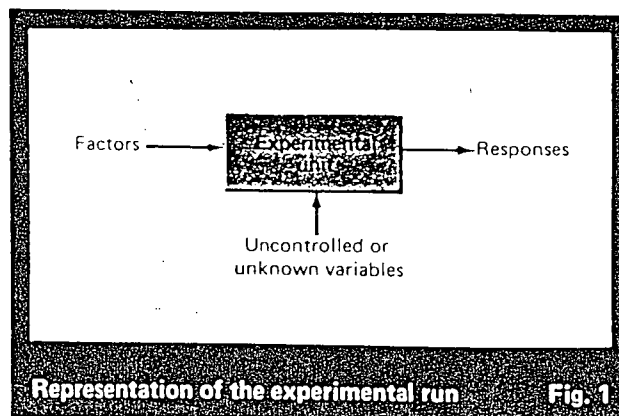
The quantal or binary response has two values, pass or fail, and this situation comes up in drug testing or in destructive physical testing such as impact strength. This response may be made semicontinuous by pooling the results of several identical experimental runs into a "percentage responding" result, but special techniques are often necessary, as described by Finney [11].

In order to design a meaningful experiment, an estimate of the response variability must be available. This information will determine the number of runs required in the design, as will be discussed later. Variability is expressed in terms of the standard deviation ( $\sigma$ ). For those unfamiliar with this concept, the standard deviation is roughly\* the average difference between responses from duplicate experiments. The standard deviation is assumed to be constant over the range of response values to be encountered during experimentation. If this can not be assumed, the following procedures can be modified to cope with the problem.

## Factor variables

Factors, or experimental variables, are controlled by the experimenter. The factor level is the value or setting of a factor during an experimental run. Like responses, they can be classified, according to measurement scale,

\*More precisely,  $\sigma$  is 88.6% of the expected difference between duplicates.



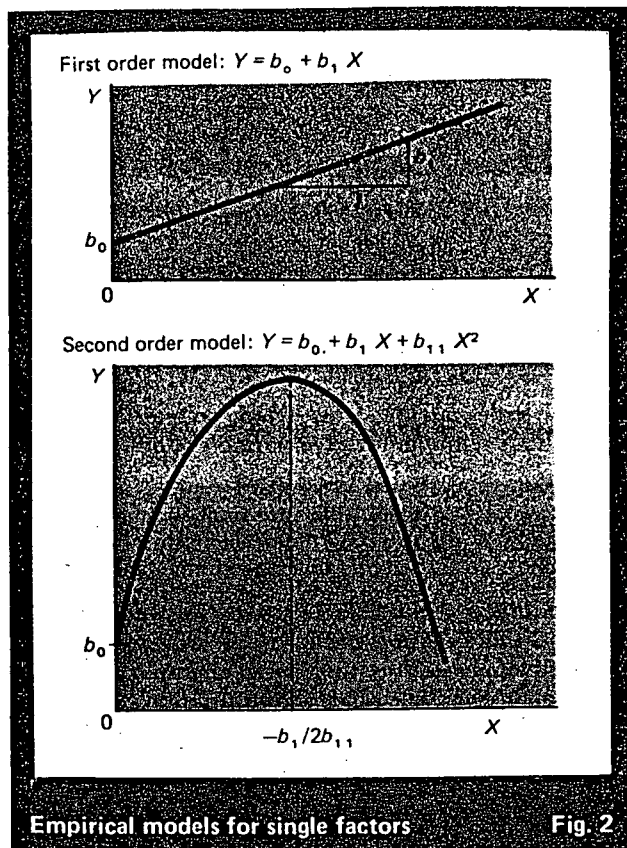


Fig. 2

as quantitative or continuous (temperature, time), or as qualitative or categorical (catalyst type, solvent). The latter are the most difficult to work with, since the measurement scale usually has no natural ordering.

When experimenters have a choice of available measurement scales, they must select the one most appropriate to the technical situation. For example, hydrogen-ion concentration can also be expressed as pH. If there are two or more factors, functional combinations of factors may be more meaningful than the original ones. For example, instead of manipulating the starting concentrations of reactants A and B, it might be more sensible to think in terms of the reactant ratio, A/B, and total reactants, A + B.

The number of potential factors will be greatest at the start of an investigation, when the least is known about the system, and will usually drop to a relative few as knowledge develops. At the start of the variable-screening phase, every effort must be made to list all factors thought to be influential. The practice of introducing new factors in the course of an investigation will not be as efficient, although it may sometimes be unavoidable.

### Mathematical models

When responses and factors are continuous in scale, it is useful to consider the factor-response relationship in terms of a mathematical function, or model. Interpretation of the experimental results will be more economical in thought and less ambiguous when considered within the discipline of the mathematical model. At the start of an investigation, when little is known about the

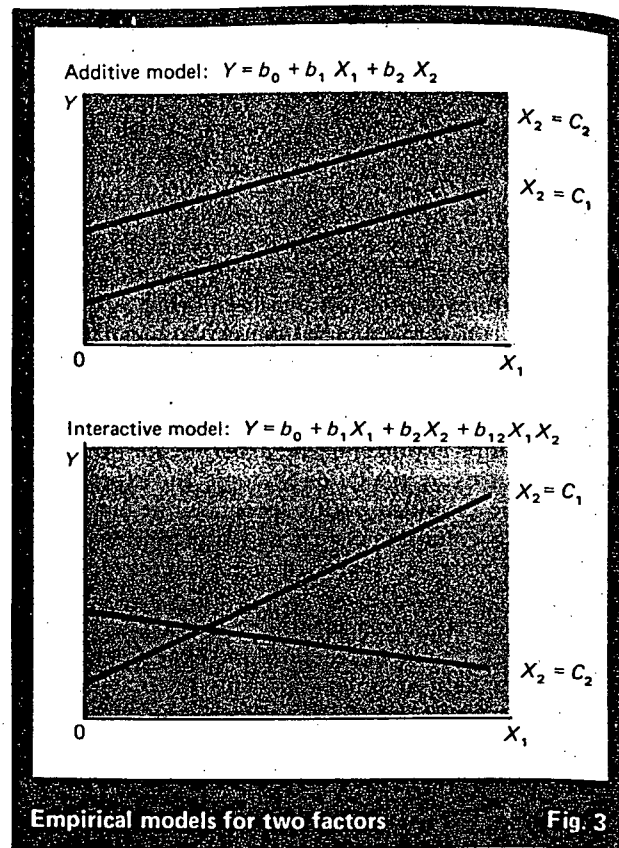


Fig. 3

true relationships, an empirical model, such as a first- or second-degree polynomial, will suffice to give rough insights. At the later stages, a theoretical model, derived from first principles, may be necessary to give the required accuracy of prediction over a wide range of conditions.

In the case of a single factor, the simplest empirical model is the first-order function:  $Y = b_0 + b_1 X$ . The model parameters,  $b_0$  and  $b_1$ , are termed the intercept and slope, respectively. This model, as pictured in Fig. 2, is useful for predicting a response  $Y$  over a limited range of the factor  $X$ . It can also be used in the variable-screening stage, where the interest is centered on the factors having largest effect on the response  $Y$ . If  $b_1$  is close to zero, we say that the factor has no significant effect on the response.

Most of us, however, tend to believe that the response-factor relationship is a continuous curve. The second-order function,  $Y = b_0 + b_1 X + b_{11} X^2$ , gives a reasonably satisfactory fit in these situations (Fig. 3). Here we wish to determine a rough optimum, located at a factor level equal to  $-b_1/2b_{11}$ , where  $b_{11}$  is termed the curvature. If  $b_{11}$  is close to zero, the response is said to be approximately first-order with respect to the factor.

For two or more factors, a complicating situation known as interaction may exist, which means that the factors do not operate independently on the response. (If independent, the factors are said to be additive.) When there is little or no curvature with respect to either factor, the simplest two-factor model is:  $Y = b_0 + b_1 X_1 + b_2 X_2 + b_{12} X_1 X_2$ . The parameters  $b_1$  and  $b_2$  are the slopes corresponding to the factors  $X_1$  and  $X_2$ .

## Nomenclature

$b_0$	Intercept term in model
$b_i$	Slope of factor $i$ in model
$b_{ii}$	Curvature of factor $i$ in model
$b_{ij}$	Interaction of factors $i$ and $j$ in model
$C$	Number of centerpoints in design
$D_i$	Main effect of dummy factor
$d$	Number of dummy variables
$N$	Number of factorial runs in design
$n$	Number of factors in design
$r$	Number of replicates of a run
$s$	Estimate of response standard deviation
$s^2$	Estimate of response variance
$t$	Student's $t$ statistic
$\nu$	Total degrees of freedom
$X_i$	Level of factor $i$
$Y$	Response value
$\bar{Y}$	Average response
$\alpha$	Distance from origin of axial or "star" point in a central composite design
$\Delta$	Minimum response change of technical interest
$\sigma$	Response standard deviation

When  $b_{12}$ , the interaction parameter, is zero, we have a strictly first-order additive model as pictured in Fig. 4. A plot of  $Y$  vs.  $X_1$  at any two constant values of  $X_2$  will be a set of two parallel straight lines.

When  $b_{12} \neq 0$ , the model is interactive. To appreciate the effect of the interaction terms, we can recast the model to emphasize the effect of  $X_2$  on the  $Y$  vs.  $X_1$  relationship:

$$Y = [b_0 + b_2 X_2] + [b_1 + b_{12} X_2] X_1$$

Intercept                      Slope

In this interactive model, the value of  $X_2$  affects the slope of the  $Y$  vs.  $X_1$  relationship, as well as the intercept. This gives rise to two nonparallel lines at two constant values of  $X_2$  (Fig. 3). Although this model is second-order in  $X_1$  and  $X_2$ , any plot of  $Y$  vs. one factor, at a constant value of the second factor, will be a straight line.

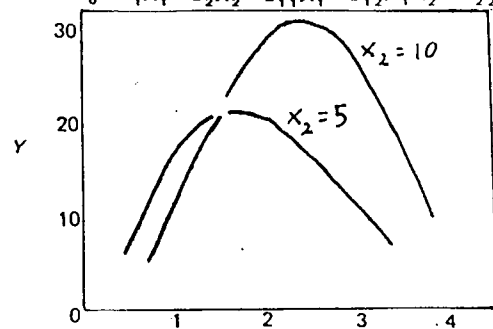
When the underlying relationship between the response and a factor is curved, then a quadratic or curvature term is added. The full second-order model in two variables is:

$$Y = b_0 + b_1 X_1 + b_2 X_2 + b_{11} X_1^2 + b_{12} X_1 X_2 + b_{22} X_2^2$$

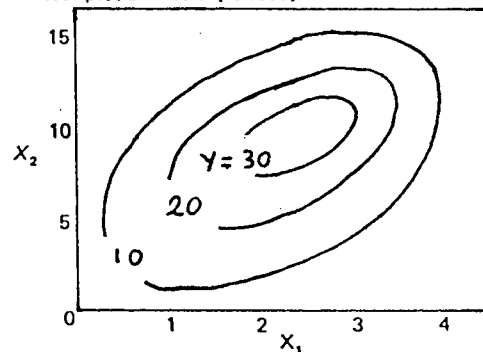
This kind of model will give an excellent description of the response within the region of experimentation, and can be used for interpolative purposes or to find a rough internal optimum, if one exists. Fig. 4 is a plot of  $Y$  vs.  $X_1$  at constant values of  $X_2$ . Another useful plot is a contour mapping of the response surface  $Y$  over the factor space defined by the values of  $X_1$  and  $X_2$  (Fig. 5). This plot indicates a maximum response near the center of the factor space. It should be emphasized, however, that second-order empirical models are very unreliable for prediction outside the range of experimentation.

Because of the good (perhaps almost too good) per-

Second-order model:  
 $Y = b_0 + b_1 X_1 + b_2 X_2 + b_{11} X_1^2 + b_{12} X_1 X_2 + b_{22} X_2^2$



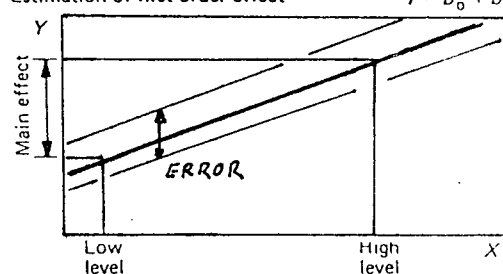
Contour plot of  $Y$  vs.  $X_1$  and  $X_2$ .



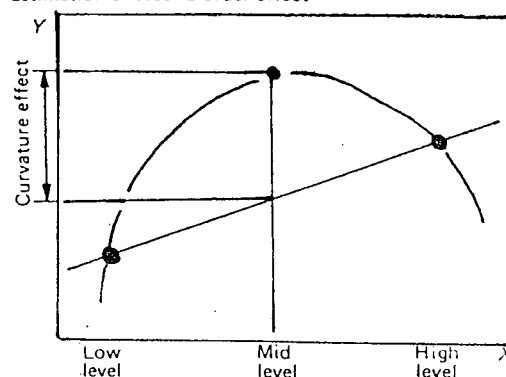
Full second-order model in two factors

Fig. 4

Estimation of first-order effect  $Y = b_0 + b_1 X$

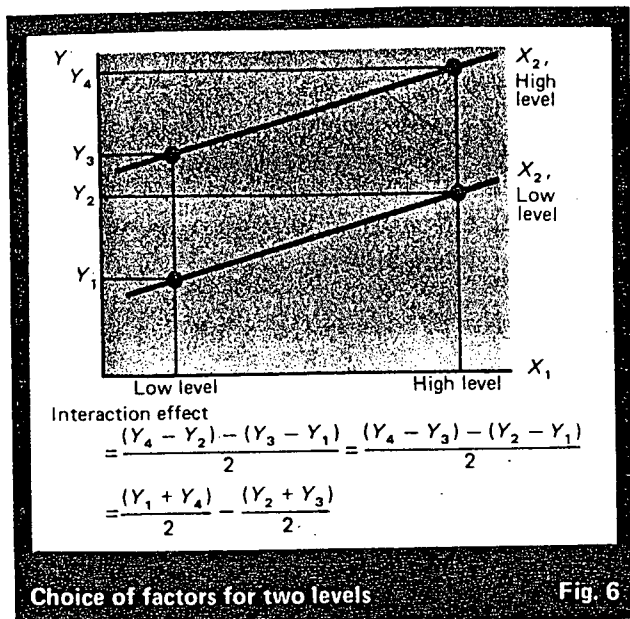


Estimation of second-order effect



Choice of factor levels for single factor

Fig. 5



formance of second-order models, it is seldom useful to consider third- or higher-order polynomials. Such models may predict several optima and may give the impression that the response behaviors are unduly complicated with respect to the factors.

For  $n$  factors, the full second-order model is

$$Y = b_0 + \sum_{i=1}^n b_i X_i + \sum_{i=1}^n \sum_{j=1}^n b_{ij} X_i X_j$$

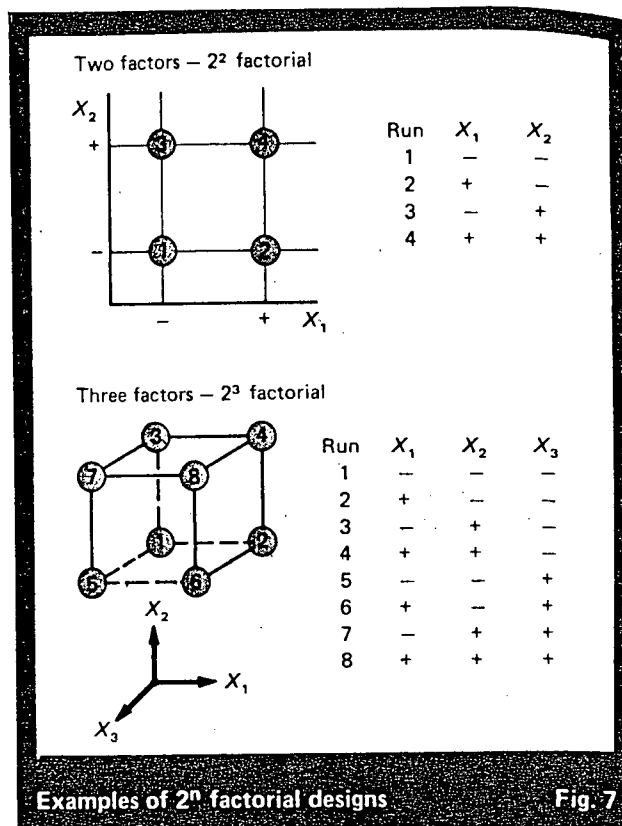
which has  $[(n+1)(n+2)/2]$  parameters to be estimated. Since this number of parameters can become large very quickly with  $n$ , a simpler model is generally assumed at the start of the investigation (such as a first-order model). As factors are eliminated by experimentation, the model can be gradually extended to partial or full second-order, or it can be replaced by a theoretical model.

For qualitative factors, there is no continuous function linking the response to the levels of a factor. It is necessary to think in terms of comparison of response between two levels of a qualitative factor, all other factors being held constant. Very often the best approach is to model each level of the qualitative factor separately in terms of the other (continuous) factors. For more than one qualitative factor, each combination of qualitative factor levels must be so considered. This illustrates the complicating aspect of using qualitative factors in the design. A statistical consultant can be of great assistance in these circumstances.

### Choice of factor levels

An experimental design consists of a set of experimental runs, with each run defined by a combination of factor levels. The choice of factor levels is influenced by the mathematical model under consideration. An experimental design is therefore determined by the number and type of factors, together with the mathematical model.

For the simplest case of a single factor and first-order



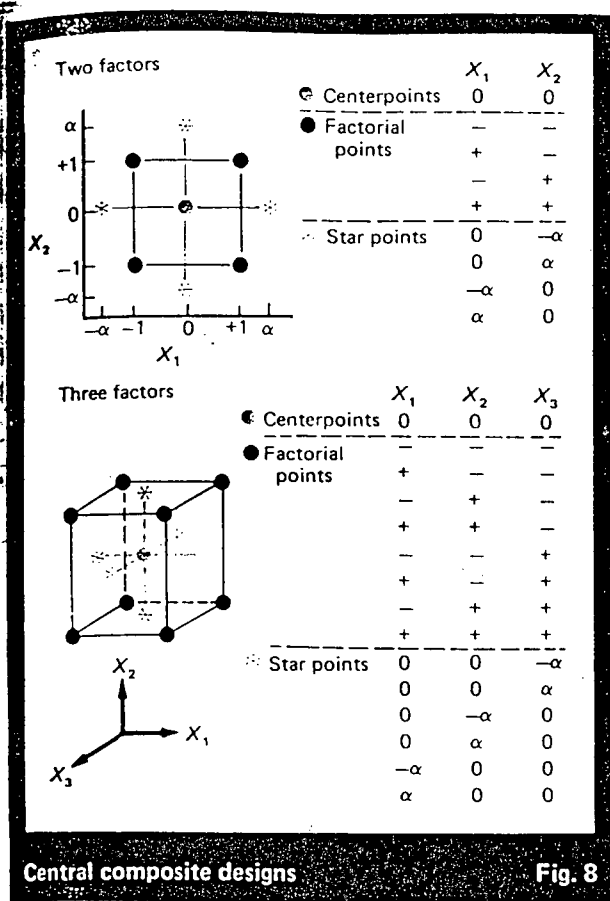
model, only two factor-levels are necessary to estimate the parameters  $b_0$  and  $b_1$ . In this discussion, these two levels will be coded as "low" and "high", or "-" and "+". The change in response between the levels is termed the factor main effect. Since random error can easily obscure the main effect if levels are set too close together, the main effect can be estimated most precisely from extreme level-settings of the factor, as shown in Fig. 5. The model slope parameter  $b_1$  is equal to the main effect divided by the difference in the actual, or uncoded, values of the factor levels. It is more advantageous, however, to work with main effects rather than slopes, since the former can be calculated more easily.

If a second-order model is under consideration, a third factor-level is required to estimate the curvature parameter  $b_{11}$ . This third level, normally run halfway between the extreme factor levels, is termed the centerpoint, and is coded as "medium" or "0". The curvature effect is defined as the difference between the experimental centerpoint response and the centerpoint value expected from a first-order model fit to the extreme points (Fig. 5).

More than 3-5 factor levels are seldom necessary when using first- or second-order empirical models. If the factor is qualitative, however, the number of factor-levels will be dictated by the experimenter. Where theoretical models are under consideration, more than three factor-levels may be necessary to choose the best among several candidate models.

For more than one factor, each experimental run is defined as a combination of factor levels. In the two-factor case, the interaction effect must be estimated in addition to the two main effects. The minimum number



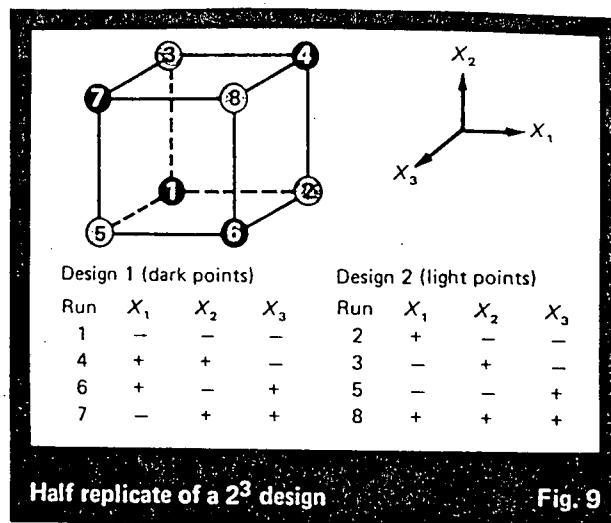


of runs will therefore be four, since we must estimate two slopes of the  $Y - X_1$  relationship and compare these slopes at two values of  $X_2$  to check on interaction. If the interaction effect is zero, the lines are parallel as in Fig. 6.

The four-run design described above is known as a  $2^2$  factorial design, and is a member of a class of designs known as  $2^n$  factorials ( $n$  factors each run at two levels with all factor-level combinations represented). These designs are useful for estimation of main effects and interactions. The factor-level combinations of the  $2^2$  and  $2^3$  designs (see Fig. 7) can be represented as the corners of a square and a cube, respectively.

Curvature effects could be estimated by adding a third level of each factor at various combinations of the remaining factors. In the early investigative stages, however, it is more economical to assess the overall curvature of the system. This can be done by the addition of one combination of all factor centerpoints, located at the centroid of the design. For  $2^2$  and  $2^3$  designs, this centerpoint run would be located at the centers of the square and cube, respectively, as shown in Fig. 7. The overall curvature effect is estimated as the difference between the response at the centerpoint and the expected response, assuming a first-order model in all factors. This expected response value is estimated from the average of the  $2^n$  points.

If significant overall curvature is detected by the centerpoint run, additional runs can be subsequently added to make separate estimates of curvature for each



factor. These additional runs (called axial or "star" points), combined with the  $2^n$  factorial plus centerpoint, form a central composite design, as illustrated in Fig. 8 for the two- and three-factor cases. The recommended level for  $\alpha$ —the distance from the centerpoint—ranges from 1 to  $2^{n/4}$ , where  $n$  is the number of factors, and the factorial points are at unit distance in each factor from the centerpoint.

A major disadvantage of  $2^n$  factorials is the large number of distinct runs required as  $n$  increases. To circumvent this problem, suitable fractions, or subsets, of the entire design can be used. It will be necessary, however, to then sacrifice some or all of the interaction estimates. Fractional  $2^n$  designs are useful in the variable-screening stage, and can be expanded to larger fractions or even full  $2^n$  designs as desired. An example of a half fraction of a  $2^3$  design is shown in Fig. 9. Either set of four runs can provide main-effect estimates for a first-order model in three factors.

In the variable-screening stage, experimental designs are built around full or fractional  $2^n$  designs with a single centerpoint. These designs are suitable for estimation of main effects and overall curvature, and, in certain cases, groups of interactions. Depending on the experimental results and the number of factors remaining, these designs can be augmented to expand the range of the existing factors, and to estimate further second-order model parameters in the optimization stage. Thus, most chemical-process investigations can take place in stages, with the experimental objectives changing in accordance with the results of the previous stage.

### Size of design

The precision of an estimate of main effect, interaction, or curvature depends on the number of data used in the estimate, together with the magnitude of the response error  $\sigma$ . In a  $2^n$  design, all the runs are used in each estimate of main effect and interaction. The experimenter must, therefore, set the total number of runs,  $N$ , required to achieve the desired precision.

To do this, the experimenter determines the minimum change in response of technical interest, denoted

by the symbol  $\Delta$ . The experiment should enable this effect to be declared statistically significant with a high degree of assurance (if it indeed exists). The relationship between  $N$  and the ratio  $\Delta/\sigma$  has been developed by statisticians, and is shown in Fig. 10. If we wish to detect an effect equal to twice the response error ( $\Delta/\sigma = 2$ ), then about 14 runs will be required. In order to detect a response change of a magnitude equal to the response error ( $\Delta/\sigma = 1$ ), a 50-run experiment will be necessary.

If  $N$  is much larger than the chosen design, based on the mathematical model, then it may be necessary to repeat, or replicate, the entire design one or more times. The primary purpose of this replication is to provide sufficient precision for the estimates. A valuable secondary purpose is to provide a more-precise estimate of  $\sigma$ , which can then be used to establish the size of succeeding designs.

### Order of experimentation

To guard against systematic trends in uncontrolled (or unknown) variables during execution of the design, it is prudent to randomize the order in which the runs are made. If the response-measurement process is conducted as a separate operation, the randomization procedure should be applied here as well. This will, of course, require coordination with the analytical group responsible for the measurements. Any random process of ordering the runs will suffice, but drawing numbers out of a container is as good a method as any.

In some cases it may be inconvenient or impractical to randomly vary the level of one or more factors, since this may require, for example, a lengthy temperature adjustment or a major mechanical change. This gives rise to a special situation known as split plotting (the term originating from agricultural experiments), and a statistician should assist in the analysis of such data.

It may also be recognized that the experimental units are not homogeneous, but may differ due to some known uncontrolled variable. This situation requires that the experimental units be segregated into blocks of homogeneous experimental units. Each block can be considered as a level of an extraneous, or blocking, variable. Examples of blocking variables are source or batch of materials, type of equipment, seasonality, people, or cages of animals. The block size is the minimum number of experimental units available in a block. If block size is greater or equal to half the runs in a full or fractional  $2^n$  design, then the blocking factor can simply be included as another factor in the design. If not, a statistician can be consulted to set up an appropriate blocking pattern. It is wise not to ignore blocking variables, for doing so can result in the inflation of the error or the mixing of the block effect with the other effects in the model.

### Recording of data

After the design is chosen, the coded low and high levels for each factor are converted to actual factor settings and listed in the experimental instructions. These should contain the experimental-run procedures, sampling procedures, and analytical documentation.

If any of the factor levels cannot be controlled pre-

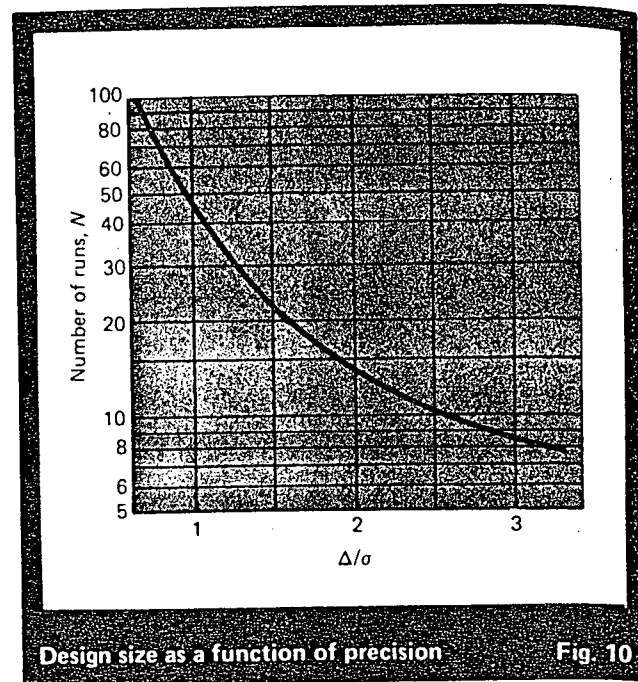


Fig. 10

cisely, but can be measured, then the actual value (or average of repeated measurements) should be taken as the factor level for statistical analysis of the experiment. Any uncontrolled variables that can be measured, and which could possibly influence the response, should also be recorded. Any unusual occurrences should also be noted, since they could explain possible anomalous response values.

### Selection of design

Many practical and statistical aspects of experimental design have been separately discussed, and these elements are now brought together to formulate a design for a specific situation. The following information should be available:

1. A list of responses to be studied, together with an estimate of each response error,  $\sigma$ .
2. A list of  $n$  factors to be studied, together with the ranges (low and high levels) for each quantitative factor, and a list of levels for each qualitative factor.
3. A statement of the problem to be investigated, together with an appropriate mathematical model.
4. The minimum number of runs ( $N$ ) needed to attain the required precision for estimates of the factor effects.
5. A check to see whether all experimental units are homogeneous; if they are not, the selection of a blocking scheme is made.

The situations of variable screening, rough optimization, and final optimization will each be considered in order.

During the variable-screening phase, the primary emphasis is on identification of the most important factors. Secondary goals will be rough detection of second-order effects (curvature and interaction), and obtaining a better estimate of  $\sigma$  (response error) for use in later investigative phases. This aim is reflected in the

Eight-run screening design

Table II

Run	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	X <sub>4</sub>	X <sub>5</sub>	X <sub>6</sub>	X <sub>7</sub>
1	-	-	-	-	+	+	+
2	+	-	-	+	+	-	-
3	-	+	-	+	-	+	-
4	+	+	-	-	-	-	+
5	-	-	+	+	-	-	+
6	+	-	+	-	-	+	-
7	-	+	+	-	+	-	-
8	+	+	+	+	+	+	+
Estimates of main effects and interactions	1	2	3	4	5	6	7
	45	35	25	15	23	13	12
	36	46	16	26	14	24	34
	27	17	47	37	67	57	56

mathematical model:  $Y = b_0 + b_1X_1 + \dots + b_nX_n$  + (overall curvature) + (interaction).

Individual interaction and curvature effects are not directly estimated, but their presence can be measured indirectly.

Some useful screening designs are given in Tables II-VI, with run sizes ranging from 8 to 24 in multiples of 4. Larger-sized designs, up to 100 runs, are given by Plackett and Burman [14]. A thorough discussion of fractional  $2^n$  designs is given by Box and Hunter [3].

Each table consists of an array of - and + values, which correspond to the low and high levels of each factor, which appear as column headings. Each row in the array defines the factor levels for a given experi-

Twelve-run screening design

Table III

Run	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	X <sub>4</sub>	X <sub>5</sub>	X <sub>6</sub>	X <sub>7</sub>	X <sub>8</sub>	X <sub>9</sub>	X <sub>10</sub>	X <sub>11</sub>
1	+	+	-	+	+	+	-	-	-	+	-
2	+	-	+	+	+	-	-	-	+	-	+
3	-	+	+	+	-	-	+	+	-	+	+
4	+	+	+	-	-	-	+	+	+	+	-
5	+	+	-	-	-	+	-	+	+	-	+
6	+	-	-	-	+	-	+	+	-	+	+
7	-	-	-	+	-	+	+	-	+	+	+
8	-	-	+	-	+	+	-	+	+	+	-
9	-	+	-	+	+	-	+	+	+	-	-
10	+	-	+	+	-	+	+	+	-	-	-
11	-	+	+	-	+	+	+	-	-	-	+
12	-	-	-	-	-	-	-	-	-	-	-

mental run. Each design can accommodate up to  $k - 1$  factors in  $k$  runs, but the usual practice is to leave 2-5 unassigned columns for groups of interactions.

The number of runs in the chosen design is compared with  $N$ , the number of runs required for precision of the estimates. If  $N$  is much larger, either the design must be replicated or a larger design must be selected from Tables II-VI to approximately attain the required  $N$  runs. For example, if  $n = 7$ , the 12-run design in Table III might be chosen. If  $N = 14$ , this design can be used, but if  $N = 23$ , either the 12-run design would have to be duplicated or the 24-run design would be selected.

Factors can be assigned to the design columns in any convenient manner. The unassigned columns, termed

Sixteen-run screening design

Table IV

Run	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	X <sub>4</sub>	X <sub>5</sub>	X <sub>6</sub>	X <sub>7</sub>	X <sub>8</sub>	X <sub>9</sub>	X <sub>10</sub>	X <sub>11</sub>	X <sub>12</sub>	X <sub>13</sub>	X <sub>14</sub>	X <sub>15</sub>
1	-	-	-	-	-	-	-	-	+	+	+	+	+	+	+
2	+	-	-	-	+	-	+	+	-	-	-	-	+	+	+
3	-	+	-	-	+	+	-	-	-	+	+	+	-	-	+
4	+	+	-	-	-	+	-	+	+	+	-	-	-	-	+
5	-	-	+	-	+	+	-	+	-	+	-	+	-	+	-
6	+	-	+	-	-	+	+	-	+	-	+	-	-	+	-
7	-	+	+	-	-	-	+	+	+	-	-	+	+	-	-
8	+	+	+	-	+	-	-	-	-	+	+	-	+	-	-
9	-	-	-	+	-	+	+	+	-	+	+	-	+	-	-
10	+	-	-	+	+	+	-	-	+	-	-	+	+	-	-
11	-	+	-	+	+	-	-	+	+	-	+	-	-	+	-
12	+	+	-	+	-	-	+	-	-	+	-	+	-	+	-
13	-	-	+	+	+	-	+	-	+	+	-	-	-	-	+
14	+	-	+	+	-	-	-	+	-	-	+	+	-	-	+
15	-	+	+	+	-	+	-	-	-	-	-	+	+	+	+
16	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Estimates of main effect and interactions	1	2	3	4	5	6	7	8	16	12	13	14	23	24	34
									45	35	25	56	15	36	26
									37	47	67	27	46	17	57
									28	68	48	38	28	58	18

Twenty-run screening design

Table V

Run	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	X <sub>4</sub>	X <sub>5</sub>	X <sub>6</sub>	X <sub>7</sub>	X <sub>8</sub>	X <sub>9</sub>	X <sub>10</sub>	X <sub>11</sub>	X <sub>12</sub>	X <sub>13</sub>	X <sub>14</sub>	X <sub>15</sub>	X <sub>16</sub>	X <sub>17</sub>	X <sub>18</sub>	X <sub>19</sub>
1	+	+	-	-	+	+	+	+	-	+	-	+	-	-	-	-	+	+	-
2	+	-	-	+	+	+	+	-	+	-	+	-	-	-	-	+	+	-	+
3	-	-	+	+	+	+	-	+	-	+	-	-	-	-	+	+	-	+	+
4	-	+	+	+	+	-	+	-	+	-	-	-	-	+	+	-	+	+	-
5	+	+	+	+	-	+	-	+	-	-	-	-	+	+	-	+	+	-	-
6	+	+	+	-	+	-	+	-	-	-	-	+	+	-	+	+	-	-	+
7	+	+	-	+	-	+	-	-	-	-	+	+	-	+	+	-	-	+	+
8	+	-	+	-	+	-	-	-	-	+	+	-	+	+	-	-	+	+	+
9	-	+	-	+	-	-	-	-	+	+	-	+	+	-	-	+	+	+	+
10	+	-	+	-	-	-	-	+	+	-	+	+	-	-	+	+	+	+	-
11	-	+	-	-	-	-	+	+	-	+	+	-	-	+	+	+	+	-	+
12	+	-	-	-	-	+	+	-	+	+	-	-	+	+	+	+	-	+	-
13	-	-	-	-	+	+	-	+	+	-	-	+	+	+	+	-	+	-	+
14	-	-	-	+	+	-	+	+	-	-	+	+	+	+	-	+	-	+	-
15	-	-	+	+	-	+	+	-	-	+	+	+	+	-	+	-	+	-	-
16	-	+	+	-	+	+	-	-	+	+	+	+	-	+	-	+	-	-	-
17	+	+	-	+	+	-	-	+	+	+	+	-	+	-	+	-	-	-	-
18	+	-	+	+	-	-	+	+	+	+	-	+	-	+	-	-	-	-	+
19	-	+	+	-	-	+	+	+	+	-	+	-	+	-	-	-	-	+	+
20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

the dummy factors, are not used to define the experimental conditions, but will come into play in the data-analysis stage. Only the columns corresponding to real factors are used to determine the experimental runs.

If qualitative factors are to be inserted into the design, this can be done at only two levels. Screening qualitative factors at more than two levels will require the help of a statistician. With qualitative factors at two levels, the assignment of - and + to the factor levels is arbitrary.

These tables represent only a small fraction of the total number of factor-level combinations that could be run. It could be possible that some of the runs given in the tables might be impractical to run, for safety or other reasons. Additionally, other runs not given in the design might be of interest. To accommodate the experimenter, these designs may be modified by changing the polarity of one or more columns in the design, i.e., switching the - and + signs in the columns. This way, a more desirable set of runs can be attained.

When the design is finished, the run order should be randomized to guard against systematic errors.

To estimate curvature and experimental error, two or more centerpoints are added to the factorial points. The centerpoints should be evenly spaced over the experimental-run order.

Following the variable-screening phase, the surviving factors are studied further in the rough optimization phase. If the system turns out to be rich in surviving factors, a statistician can be consulted to set up the more-complex design that will be required to estimate the large number of interaction effects.

During the rough optimization phase, it is advisable to estimate all factor main-effects and interactions in order to determine the direction of the optimum response. The estimation of overall curvature and experi-

mental error are secondary goals. The interactive mathematical model applies:

$$Y = b_0 + b_1X_1 + \dots + b_nX_n + b_{12}X_1X_2 + \dots + b_{mn}X_mX_n + (\text{overall curvature})$$

where  $m = n - 1$ . Individual curvature effects are not directly estimated.

The proper designs for this phase are full or fractional  $2^n$  designs plus centerpoints. Table II can be used as a full  $2^3$  design or a  $1/2$  fraction of a  $2^4$  design (8 runs). Table IV can be used as a full  $2^4$  design or a  $1/2$  fraction of a  $2^5$  design (16 runs). To use these tables for this phase, the factors can be assigned to the columns indicated in the legend below the design array, and this will also give the columns corresponding to interaction estimates.

In many cases the screening design can itself be the first rough optimization design, and can be reanalyzed in terms of the surviving factors. An example of this will be given in the analysis part of this article.

If the optimal response is indicated to lie outside the experimental region, then additional designs at new levels will have to be run to locate the region of the optimum. As this process proceeds, the curvature estimates will generally increase to a maximum relative to the main effects, in the optimal region.

The final optimization phase will require a full quadratic model to accurately predict the point of optimal response:

$$Y = b_0 + b_1X_1 + \dots + b_nX_n + b_{11}X_1^2 + \dots + b_{nn}X_n^2 + b_{12}X_1X_2 + \dots + b_{mn}X_mX_n$$

where  $m = n - 1$ . All of the terms in the model will be estimated.

The type of design used in this phase is the central composite design, which is basically an augmented  $2^n$

Twenty-four-run screening design

Table VI

Run	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	X <sub>4</sub>	X <sub>5</sub>	X <sub>6</sub>	X <sub>7</sub>	X <sub>8</sub>	X <sub>9</sub>	X <sub>10</sub>	X <sub>11</sub>	X <sub>12</sub>	X <sub>13</sub>	X <sub>14</sub>	X <sub>15</sub>	X <sub>16</sub>	X <sub>17</sub>	X <sub>18</sub>	X <sub>19</sub>	X <sub>20</sub>	X <sub>21</sub>	X <sub>22</sub>	X <sub>23</sub>
1	+	+	+	+	+	-	+	-	+	+	-	-	+	+	-	-	+	-	+	-	-	-	-
2	+	+	+	+	-	+	-	+	+	-	-	+	+	-	-	+	-	+	-	-	-	-	-
3	+	+	+	-	+	-	+	+	-	-	+	-	+	-	-	+	-	+	-	-	-	-	+
4	+	+	-	+	-	+	+	-	-	+	+	-	-	+	-	+	-	-	-	-	-	+	+
5	+	-	+	-	+	+	-	-	+	+	-	-	+	-	+	-	-	-	-	-	+	+	+
6	-	+	-	+	+	-	-	+	+	-	-	+	-	+	-	-	-	-	+	+	+	+	+
7	+	-	+	+	-	-	+	+	-	-	+	-	+	-	-	-	-	+	+	+	+	+	+
8	-	+	+	-	-	+	+	-	-	+	-	+	-	-	-	+	+	+	+	+	+	-	+
9	+	+	-	-	+	+	-	-	+	-	+	-	-	-	+	+	+	+	+	+	-	+	-
10	+	-	-	+	+	-	-	+	-	+	-	-	-	-	+	+	+	+	+	-	+	-	+
11	-	-	+	+	-	-	+	-	+	-	-	-	-	-	+	+	+	+	+	-	+	-	+
12	-	+	+	-	-	+	-	+	-	-	-	-	-	+	+	+	+	+	-	+	-	+	+
13	+	+	-	-	+	-	+	-	-	-	-	+	+	+	+	+	+	-	+	-	+	+	-
14	+	-	-	+	-	+	-	-	-	-	+	+	+	+	+	-	+	-	+	+	-	-	-
15	-	-	+	-	+	-	-	-	-	+	+	+	+	+	-	+	-	+	+	-	-	-	+
16	-	+	-	+	-	-	-	-	+	+	+	+	+	-	+	-	+	+	-	-	+	+	+
17	+	-	+	-	-	-	-	+	+	+	+	+	-	+	-	+	+	-	-	+	+	-	-
18	-	+	-	-	-	-	+	+	+	+	+	-	+	-	+	+	-	-	+	+	-	-	-
19	+	-	-	-	-	+	+	+	+	+	-	+	-	+	+	-	-	+	+	-	-	-	+
20	-	-	-	-	+	+	+	+	+	-	+	-	+	+	-	-	+	+	-	-	+	-	+
21	-	-	-	+	+	+	+	+	-	+	-	+	+	-	-	+	+	-	-	+	-	+	+
22	-	-	+	+	+	+	+	-	+	-	-	+	+	-	-	+	+	-	-	+	-	+	-
23	-	+	+	+	+	+	-	+	-	+	+	-	-	+	+	-	-	+	-	+	-	-	-
24	-	-	-	-	-	-	-	-	-	-	-	-	-	+	+	-	-	+	-	+	-	-	-

factorial plus centerpoints. The additional runs are solely for the purpose of estimating the curvature terms for each factor. Examples of central composite designs are shown in Fig. 8 for two and three factors. Another useful class of designs for this purpose is described by Box and Behnken [2].

### Example

An oversimplified example summarizes the experimental design process. The piloting of a new batch catalytic process for chemical *Q* is in the beginning stages of investigation. It is assumed that the only response of interest is the reaction yield, a continuous variable. It is estimated from the prior bench study that the yield variability,  $\sigma$ , is about 2% yield.

Four factors have been proposed for the variable-screening phase, together with their factor-level ranges:

Reaction temperature	X <sub>1</sub>	70-80°C
Reactant ratio	X <sub>2</sub>	1.05-1.35
Reaction time	X <sub>3</sub>	1-2 h
Catalyst level	X <sub>4</sub>	0.05-0.08%

All four factors are quantitative, and the extremes of these ranges are picked as the low and high factor levels.

Since the objective is to estimate main effects, the appropriate mathematical model is

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + \text{(overall curvature)}$$

Based on past experience with such systems, the likelihood is that these factors may be interactive. Therefore,

it is advisable to choose a design that will at least detect the existence of such interactions.

Economics of this situation dictate that a 6-8% yield increase would be of vital interest in this study.  $\Delta = 6\%$  is chosen as the response difference to be detected with a high degree of assurance. Entering Fig. 8 with a  $\Delta/\sigma$  value of  $6/2 = 3$ , it is seen that about  $N = 8$  runs will be required.

The experimental unit in this case will consist of a batch of materials in a reactor. The same reactor will be used for all runs, and there is sufficient material for at least 25 runs. The experimental units will, therefore, be homogeneous, and no blocking variables will be used.

With four factors, an eight-run design from Table II

Chemical *Q* — factorial runs

Table VII

Run	Reaction temperature, C	Reactant ratio	Reaction time, h	Catalyst concentration, g/L
1	70	1.05	1	0.05
2	80	1.05	1	0.08
3	70	1.35	1	0.08
4	80	1.35	1	0.05
5	70	1.05	2	0.08
6	80	1.05	2	0.05
7	70	1.35	2	0.05
8	80	1.35	2	0.08

**Chemical Q — complete design after  
run-order randomization**

**Table VIII**

Run	Reaction temperature, °C	Reactant ratio	Reaction time, h	Catalyst concentration, g/L	Original run no.*
1	75	1.20	1.5	0.065	cp
2	70	1.35	1.0	0.08	3
3	80	1.05	2.0	0.05	6
4	80	1.35	1.0	0.05	4
5	70	1.35	2.0	0.05	7
6	75	1.20	1.5	0.065	cp
7	70	1.05	2.0	0.08	5
8	80	1.05	1.0	0.08	2
9	80	1.35	2.0	0.08	8
10	70	1.05	1.0	0.05	1
11	75	1.20	1.5	0.065	cp

\*Original run number from Fig. 12; cp = centerpoint.

will be satisfactory. Assigning columns  $X_1$  through  $X_4$  to the four factors, three columns are left over for dummy factors to estimate interaction. After substituting the actual factor levels in place of the — and + values in Table II, the design layout is as shown in Table VII.

The decision is made to run three centerpoints to estimate overall curvature and response error. The centerpoints of the factor levels  $X_1$  through  $X_4$  are:

Temperature	75°C
Reactant ratio	1.20
Reaction time	1.5 h
Catalyst level	0.065%

The three centerpoint runs will be made at the above factor settings.

The eight factorial runs are randomized by drawing the run numbers 1–8 from a container and running them in the order drawn. The centerpoints are run as the first, middle and last run of the design. If the factorial run order were randomized as 3, 6, 4, 7, 5, 2, 8, 1, then the overall design would appear as in Table VIII.

This example will be used in the following section on analysis of designed experiments.

### Analysis of designed experiments

Analysis of statistically designed experiments is reasonably straightforward because of the balanced nature of the designs. This part of the article will outline the calculations for estimation of response error, factor main-effects, interaction and overall curvature, and assessment of their statistical significance. These can be easily accomplished using a calculator. Such other techniques, as regression analysis and contour plotting, which require the availability of a computer, will be mentioned. For basic information on statistical analysis, see Dixon and Massey [9] and Natrella [13]. A useful compendium of statistical tables and experimental designs can be found in the CRC Statistics Handbook [1].

### Estimation of response error using replicates

Response error can be estimated either directly from replicate runs, or indirectly using dummy factors.

If  $Y_1, \dots, Y_r$  represent the response values resulting from  $r$  replicate runs, then an estimate  $s$  of the response standard deviation  $\sigma$  can be calculated as follows:

$$s = \sqrt{\Sigma(Y_i - \bar{Y})^2 / (r - 1)}$$

where  $\bar{Y} = \Sigma Y_i / r$  is the average response, and  $\Sigma$  represents the sum over  $i$  from 1 to  $r$ . Another formula may be more convenient to use with some calculators.

$$s = \sqrt{\Sigma Y_i^2 - r\bar{Y}^2 / (r - 1)}$$

where  $\Sigma Y_i^2$  is the sum of the squared responses. The number  $(r - 1)$  is termed the degrees of freedom of the error estimate.

In the case of duplicates ( $r = 2$ ), the formula is reduced to:

$$s = \sqrt{(Y_1 - Y_2)^2 / 2}$$

Replicates are available from two sources in designed experiments: centerpoint replication, and factorial point replication. Centerpoints can and should be replicated two or more times in each designed experiment. This will provide greater precision for the overall curvature estimate, as well as an estimate of response error. Factorial points will only be replicated when an entire design is replicated to provide the required precision on estimates of main effects and interactions.

To illustrate the use of these formulas, suppose that as a result of this article's designed experiment, the three centerpoint yields of chemical Q had been 75, 80 and 76%.

The average and standard deviation are calculated as follows:

$$\bar{Y} = \Sigma Y_i / r = (75 + 80 + 76) / 3 = 77\% \text{ yield}$$

$$s = \sqrt{[(75 - 77)^2 + (80 - 77)^2 + (76 - 77)^2] / (3 - 1)} = 2.6\% \text{ yield}$$

with  $(r - 1) = (3 - 1) = 2$  degrees of freedom.

Error estimates from several sources may be combined, or pooled, for a firmer estimate of error. The pooled estimate is a weighted average of the variances (or squares of the standard deviations), weighted by their respective degrees of freedom (df). The pooled variance for  $k$  separate estimates of error,  $s_i$ , each with  $r_i$  replicates, is:

$$s^2 = \Sigma(r_i - 1)s_i^2 / \Sigma(r_i - 1)$$

where  $\Sigma$  denotes the summation over  $i$  from 1 to  $k$ . The symbol  $\nu$  may be used for the total degrees of freedom,  $\nu = \Sigma(r_i - 1)$ .

To exemplify the pooling calculation, it is assumed that two reactions of chemical Q at some other fixed condition had been previously run, with yields of 52% and 50%.

Data source	Responses	$s^2$	$r$
Previous	52, 50	2	2
Centerpoints	75, 80, 76	7	3

$$s^2 = [(r_1 - 1)s_1^2 + (r_2 - 1)s_2^2] / [(r_1 - 1) + (r_2 - 1)]$$

$$= [(1)(2) + (2)(7)] / [1 + 2] = 16/3 = 5.33$$

$$s = \sqrt{5.33} = 2.3$$

The new estimate of response error is 2.3% yield with 3

Run no.	Yield response	Temperature $X_1$	Ratio $X_2$	Time $X_3$	Catalyst concentration $X_4$	Dummy factors $X_5$	$X_6$	$X_7$
1	58	—	—	—	—	+	+	+
2	83	+	—	—	+	+	—	—
3	62	—	+	—	+	—	+	—
4	77	+	+	—	—	—	—	+
5	75	—	—	+	+	—	—	+
6	84	+	—	+	—	—	+	—
7	75	—	+	+	—	+	—	—
8	86	+	+	+	+	+	+	+
$\Sigma +$	660	330	300	320	306	302	290	296
$\Sigma -$		270	300	280	294	298	310	304
Difference		60	0	40	12	4	-20	-8
Effect	75	15	0	10	3	1	-5	-2

degrees of freedom—two degrees from the centerpoint estimate, and one degree from the previous runs.

### Estimation of main effects

Tables II–VI have the following features in common:

1. Half the runs of each factor are at the low level, and half are at the high level.
2. Each factor is “balanced” with respect to the other factor in that both the low- and high-level runs of any factor are evenly split between low and high levels of all other factors.

Recalling that a main effect is estimated from the difference between the average high- and low-factor-level responses:

Main effect of  $X_i =$

$$\frac{\Sigma(\text{responses at high } X_i) - \Sigma(\text{responses at low } X_i)}{(\text{half the number of factorial runs})}$$

Thus, all the data in an experiment are used to estimate each main effect, and each main effect is estimated independently of the other main effects. This feature of  $2^n$  designs is known as hidden replication, giving maximum information per experimental run. In poorly planned designs, only a subset of the runs is used for each estimate.

A calculation procedure for the main effects is now set up and illustrated, using the hypothetical chemical-Q experiment. It is assumed that the yields from the factorial runs resulted in the data shown in Table IX. Note that the run order is the same as in Table II.

The calculation procedure is as follows:

1. Copy the “—” and “+” factor level array from the design table (Tables II–VI).
2. List the responses in a separate column, corresponding to the run that generated it. If replicates have been run, list the average response in this column.
3. Set up additional rows labeled  $\Sigma +$ ,  $\Sigma -$ , Difference, and Effect, at the bottom of the array.
4. Sum the values in the Response column and enter the total in the  $\Sigma +$  row of this column. Divide by the number of runs in the design table and enter this value

(which is the average response) in the Effect row of the Response column.

5. For each factor column:

(a) Sum the responses corresponding to the “+” entries and enter in the  $\Sigma +$  row.

(b) Sum the responses corresponding to the “—” entries and enter in the  $\Sigma -$  row.

(c) Subtract the  $\Sigma -$  entry from the  $\Sigma +$  entry and enter in the Difference row.

(d) Divide the difference entry by one-half the number of runs in the design table, and enter this result in the Effect row. This value is the main effect for that factor.

(e) Mentally add the  $\Sigma +$  and  $\Sigma -$  entries. The sum should equal the response total under the Response column.

For example, the temperature main effect is the response average of runs 2, 4, 6, 8 (high temperature) minus the response average of runs 1, 3, 5, 7 (low temperature). The calculation is:

$$\text{Temperature effect} = \frac{(83 + 77 + 84 + 86) - (58 + 62 + 75 + 75)}{4} = 15\% \text{ yield}$$

Therefore, the effect of increasing the temperature from 70°C to 80°C averaged over all levels of reactant ratio, catalyst level and time, is to raise the yield 15%.

Also, the time effect is 10% yield, and the effects of the other two factors are much smaller, at 0 and 3% for reactant ratio and catalyst level, respectively.

The effects of the dummy factors can be similarly calculated. The factors are a measure of any interactions in the system. Since the dummy-factor estimates are 1, -5, and -2% yield, no overwhelming interaction effects are seen, but the single -5 value alerts to the possible presence of interactions.

### Assessment of significance of main effects

The effects just estimated are point estimates. They give no idea of the reliability or precision of these estimates. The precision is generally stated in the form

Original data		Yield, %	
Temperature	Time	Replicates	Average
70	1	58,62	60
80	1	83,77	80
70	2	75,75	75
80	2	84,86	85

Calculations					
Run	Yield response, %	Temperature X <sub>1</sub>	Time X <sub>2</sub>	Interaction X <sub>1</sub> X <sub>2</sub>	Variance s <sup>2</sup>
1	60	—	—	+	8
2	80	+	—	—	18
3	75	—	+	—	0
4	85	+	+	+	2
Σ +	300	165	160	145	28 (Total variance)
Σ —		135	140	155	
Difference		30	20	—10	7 (Average variance)
Effect	75	15	10	5	

## Pooled variance

$$S^2 = [(3)(5.33) + (4)(7.00)] / 7 = 43.99 / 7 = 6.28$$

$$S^2 = 2.5 \text{ with 7 degrees of freedom}$$

## 95% confidence intervals

$$ts / \sqrt{N/4} = (2.365)(2.5) / \sqrt{2} = 4.2$$

$$\text{Temperature: } 15 \pm 4.2 \text{ or } 10.8 \text{ to } 19.2$$

$$\text{Time: } 10 \pm 4.2 \text{ or } 5.8 \text{ to } 14.2$$

$$\text{Interaction: } -5 \pm 4.2 \text{ or } -9.2 \text{ to } -0.8$$

of a confidence interval, which is an interval said to include the "true" effect at a stated confidence level. The most common confidence levels are 90, 95 and 99%. The confidence-interval width is a function of the response error estimate, the number of data in the estimate, and the number of degrees of freedom in the response error estimate for a main effect. The confidence interval is:

$$(\text{Main effect estimate}) \pm ts / \sqrt{N/4}$$

where  $s$  = response error estimate with  $\nu$  degrees of freedom;  $N$  = number of factorial runs in the design; and  $t$  = student's  $t$  statistic with  $\nu$  degrees of freedom at stated confidence level. Values of the multiplier  $t$  are given in Table XI, indexed by the confidence level and the number of degrees of freedom corresponding to the estimate  $s$ .

If the confidence interval does not include zero, it can be said that the effect is significantly different from zero at the stated confidence level.

The chemical Q example had an estimate of  $s = 2.3$  with  $\nu =$  three degrees of freedom, two degrees of freedom from the three centerpoints, and one degree of freedom from two previously run pilot experiments. If a 95% confidence level is desired, the  $t$  value from Table

XI for 95% confidence and  $\nu = 3$  is 3.182. To determine the confidence intervals from the  $N = 8$ -run design:

$$ts / \sqrt{N/4} = (3.182)(2.3) / \sqrt{2} = 5.2$$

Therefore, the 95% confidence intervals are:

X <sub>1</sub> temperature	15 ± 5.2, or	9.8 to 20.2
X <sub>2</sub> reactant ratio	0 ± 5.2, or	-5.2 to 5.2
X <sub>3</sub> catalyst level	10 ± 5.2, or	4.8 to 15.2
X <sub>4</sub> time	3 ± 5.2, or	-2.2 to 8.2
X <sub>5</sub> dummy	1 ± 5.2, or	-4.2 to 6.2
X <sub>6</sub> dummy	-5 ± 5.2, or	-10.2 to 0.2
X <sub>7</sub> dummy	-2 ± 5.2, or	-7.2 to 3.2

Since all of these effects but temperature and time include zero in the confidence interval, it can be stated that the remaining effects are not significant at the 95% confidence level. Note, however, that  $X_6$  is almost significant, which alerts to the possibility of either an  $X_1X_3$  or an  $X_2X_4$  interaction in the chemical Q reaction. These two interactions correspond to  $X_6$  in the legend appearing under the design in Table II.

## Estimation of interaction effects

The calculation for interaction effects follows the same procedure as that for main effects. The interaction effect is calculated as the average response difference between one half of the factorial runs and the other half. The design table must first be augmented to include columns for interactions. An interaction column is formed from the columns of the two factors that comprise the interaction, by multiplying the entries in the factor columns. In the example of a 2<sup>2</sup> design given below, the  $X_1X_2$  column is the product of the  $X_1$  and  $X_2$  columns.

Run	X <sub>1</sub>	X <sub>2</sub>	X <sub>1</sub> X <sub>2</sub>	Response
1	—	—	+	Y <sub>1</sub>
2	+	—	—	Y <sub>2</sub>
3	—	+	—	Y <sub>3</sub>
4	+	+	+	Y <sub>4</sub>

The interaction effect is calculated as:

$$[(Y_1 + Y_4) - (Y_2 + Y_3)] / 2 \quad (\text{see Fig. 6})$$

Returning to the chemical Q example, suppose it had been decided to rule out the existence of the catalyst and reactant ratio factors, and reanalyze the design as a 2<sup>2</sup> factorial, replicated twice. Table X shows the original data and the calculations of the temperature and time main effects, together with the temperature-time interaction. It can now be seen that the  $X_1X_2$  interaction corresponds to the dummy variable  $X_6$  in the screening design.

Since the design is now considered as a 2<sup>2</sup> in duplicate, there are four sets of "duplicate" responses that can be used to estimate response error. For each temperature-time combination, the average variance  $s^2$  can be calculated and shown in the variance column in Table X. The average variance estimate is 7 ( $s = 2.6$ ) with 4 degrees of freedom (one for each set of duplicates). This estimate can be pooled with the previous 3 degrees of freedom estimate of error (Table X) to result in an estimate of  $s = 2.5\%$  yield with 7 degrees of freedom.



Two-sided student's *t* statistic

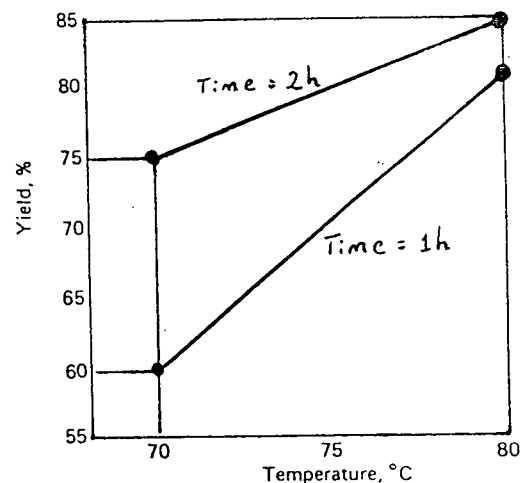
Table XI

Degrees of freedom	100 (1- $\alpha$ ) % confidence level		
	90%	95%	99%
1	6.314	12.706	63.657
2	2.920	4.303	9.925
3	2.353	3.181	5.841
4	2.132	2.776	4.604
5	2.015	2.571	4.032
6	1.943	2.447	3.707
7	1.895	2.365	3.499
8	1.860	2.306	3.355
9	1.833	2.262	3.250
10	1.812	2.228	3.169
11	1.796	2.201	3.106
12	1.782	2.179	3.055
13	1.771	2.160	3.012
14	1.761	2.145	2.977
15	1.753	2.131	2.947
16	1.746	2.120	2.921
17	1.740	2.110	2.898
18	1.734	2.101	2.878
19	1.729	2.093	2.861
20	1.725	2.083	2.845
21	1.721	2.080	2.831
22	1.717	2.074	2.819
23	1.714	2.069	2.807
24	1.711	2.064	2.797
25	1.708	2.060	2.787
26	1.706	2.056	2.779
27	1.703	2.052	2.771
28	1.701	2.048	2.763
29	1.699	2.045	2.756
30	1.697	2.042	2.750
40	1.684	2.021	2.704
60	1.671	2.000	2.660
120	1.658	1.980	2.617
$\infty$	1.645	1.960	2.576

Confidence intervals can now be set up for each main effect and interaction, and these are also shown in Table X. The conclusion is that the effect of temperature and time are statistically significant, but that their interaction is significant also. The yield increase due to an increase in the time from 1 to 2 h is greater at 70°C than at 80°C, as can be seen graphically in Fig. 11.

### Estimation of response error using dummy variables

In the absence of interactions, the comparison of the high and low levels of dummy factors do not measure any factor effects, and should have an expected value of zero. They will not always be equal to zero, in any given experiment, because of response error. Therefore,



Chemical Q—yield vs. temperature and time Fig. 11

dummy-factor effects can be used as a measure of response error.

If  $D_i$  represents the main effect of the  $i^{\text{th}}$  dummy factor, as calculated by the standard method, then an estimate of response error resulting from  $d$  dummy factors is:

$$s = \sqrt{N(\sum D_i^2)/4d}$$

where  $N$  is the number of factorial runs in the design, and  $\sum$  is the sum over  $i$  from 1 to  $d$ . This value will usually be an overestimate of  $\sigma$  because of the presence of interactions, and therefore should only be used if it is the only error estimate available. It is preferable to use replicates to estimate response error.

In the chemical Q example, the three dummy-factor main effects were 1, -5 and -2, leading to the estimate:

$$s = \sqrt{(8)(1 + 25 + 4)/(4)(3)} = \sqrt{20} = 4.5\% \text{ yield}$$

This estimate is almost twice the estimate obtained from pooled replicates. Remembering that the second dummy factor was also the time-temperature interaction, it could be removed as a dummy factor and recalculated:

$$s = \sqrt{(8)(1 + 4)/(4)(2)} = \sqrt{5} = 2.3\% \text{ yield}$$

This is much closer to the estimate that is based on replicates.

### Estimation of curvature effects

If all effects are first-order and interactive, the expected value of the response at the centroid of the design is estimated by the average of the responses of the factorial runs. The curvature effect is then estimated as the difference between the average of the centerpoint responses and the average of the factorial points. In the chemical Q example, the centerpoints averaged 77% yield, and the factorial points averaged 75% yield, giving a curvature effect of +2% yield.

A confidence interval for the curvature effect is calculated as:

$$\text{Curvature effect} \pm ts \sqrt{\frac{1}{N} + \frac{1}{C}}$$

where  $C$  = number of centerpoints, and  $N$  = the number of factorial points in the design.

In the chemical  $Q$  example,  $N = 8$  and  $C = 3$ :

$$ts \sqrt{\frac{1}{N} + \frac{1}{C}} = (2.365)(2.5) \sqrt{\frac{1}{8} + \frac{1}{3}} = 4.0$$

so that the 95% confidence interval on curvature is:  $2.0 \pm 4.0$ , or  $-2.0$  to  $6.0$ , which is not statistically significant at 95% confidence.

### Estimation for the full second-order model

The terms in the full second-order model are estimated through a regression analysis program, which is available on most computer program packages. In these calculations the actual factor levels are used, rather than the nominal values. This is particularly useful when the actual factor levels differ from the nominal levels because of control problems.

A contour-plotting program can translate the model equations into maps of the response values over two-dimensional slices of the factor space. Such maps can be useful for reconciling two responses, by overlaying of the response surfaces. We will not be able to go into the details of these programs here, but would recommend the textbook by Draper and Smith [10] as a reference for further study.

### Further design topics

A complicating situation in experimental design arises when some or all of the factors are subject to constraints. An example of this is when the factors represent components of a mixture, such as an alloy or a blend of feedstocks. This gives rise to the class of mixture designs described in articles by Cornell [5], and Snee and Marquardt [15]. These designs are useful for estimating prediction models for describing responses over the allowable composition range.

There are a number of graphical techniques in use for data analysis, but a very useful one is the half-normal plot, discussed by Daniel [7]. These plots can be used for factorial designs where there is no replication and no prior estimate of error.

### Conclusion

Although the principles of experimental design presented in this article can be put to immediate use, only the basics have been touched upon here. If your location does not have access to a statistical consultant, you might consider attending a short course in experimental design, or reading such textbooks as Cochran and Cox [6], Davies [8], or Hicks [12].

One criticism of statistical design is that the experimenter is committed to a seemingly large number of runs at the outset of an investigation. However, it is not uncommon for experimenters using a piecemeal approach to ultimately generate a larger number of runs than would have been suggested by the experimental

design. Further, if it becomes apparent that a design is being run in the wrong experimental region, there is nothing to prevent its termination.

Many experimenters do not take into consideration their experimental and measurement errors. The common sin is to base a conclusion on too few runs, only to find that the result cannot be confirmed in a later stage of the investigation. Those who measure their response error have a good feel for the reliability of their data. They know when additional experimentation may be required to "nail down" a conclusion.

Use of a mathematical model helps the experimenter to draw conclusions in a meaningful way. The concept of factor interaction is very helpful in unraveling fairly complex relationships between the response and several factors. In chemical investigations, interactions are the rule, not the exception.

The balanced nature of a statistical design lends itself to an organized approach to experimentation and a straightforward means of data analysis. Graphical aids work very well with results from designed experiments.

Even with these advantages, it should be emphasized that statistical design is a tool, a means to an end. It will not replace sound technical judgment or creativity in experimental work. Nonetheless, it is an important tool, which you, the experimenter, cannot afford to ignore.

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## **APPENDIX D**

### **SUMMARY AND FACTORIAL ANALYSIS OF EXPERIMENTAL RESULTS**

UNCATALYZED BLEACHING RUNS

Substitution	pH	Temperature (°C)	Catalyst Charge (wt.%)	Thiosulfate Titrant (ml)	[ClO <sub>3</sub> ] (mM)
50	4	50	n/a	43.80	0.73
100	3	50	n/a	23.55	0.39
75	3.2	50	n/a	59.15	0.99

CENTRE POINT RUNS

Run Number	Substitution (% eq. Cl <sub>2</sub> )	pH	Temperature (°C)	Catalyst Charge (wt.%)	Thiosulfate Titrant (ml)	[ClO <sub>3</sub> ] (mM)
1	75	3	75	0.005	20.5	0.34
6	75	3	75	0.005	20.45	0.34
14	75	3	75	0.005	19.60	0.33
20	75	3	75	0.005	21.45	0.36

# FINAL RESULTS AND FACTORIAL ANALYSIS OF EXPERIMENTAL PROGRAM 1

WORKSHEET FOR MAIN EFFECTS

Run Number	Substitution (% eq. Cl <sub>2</sub> )	pH	Temperature (°C)	Catalyst Charge (wt.%)	Substitution	pH	Temperature	Catalyst Charge	Thiosulfate Titrant (ml)	[ClO <sub>3</sub> ] (mM)	Reduction (%)
2	100	2	80	0.001	1	-1	1	-1	14.25	0.24	38.50
3	50	4	70	0.001	-1	1	-1	-1	33.90	0.57	-4.59
4	50	4	80	0.01	-1	1	1	1	2.20	0.04	93.69
5	100	4	70	0.01	1	1	-1	1	20.25	0.34	12.61
7	50	4	70	0.01	-1	1	-1	1	10.60	0.18	57.11
8	50	2	80	0.01	-1	-1	1	1	2.05	0.03	95.19
9	100	2	80	0.01	1	-1	1	1	3.15	0.05	86.41
10	100	2	70	0.001	1	-1	-1	-1	28.30	0.47	-22.13
11	50	4	80	0.001	-1	1	1	-1	15.30	0.26	28.55
12	50	2	80	0.001	-1	-1	1	-1	11.40	0.19	34.25
13	100	4	80	0.001	1	1	1	-1	15.43	0.26	33.41
15	100	2	70	0.01	1	-1	-1	1	16.50	0.28	28.79
16	50	2	70	0.01	-1	-1	-1	1	15.18	0.25	77.49
17	100	4	70	0.001	1	1	-1	-1	28.20	0.47	-21.70
18	50	2	70	0.001	-1	-1	-1	-1	33.40	0.56	15.00
19	100	4	80	0.01	1	1	1	1	7.05	0.12	69.58

FINAL RESULTS AND FACTORIAL ANALYSIS OF EXPERIMENTAL PROGRAM

WORKSHEET FOR INTERACTION EFFECTS

Run Number	Substitution (% eq. Cl <sub>2</sub> )	pH	Temperature (°C)	Catalyst Charge (wt.%)	temp/cat	pH/cat	sub/cat	pH/temp	pH/sub	temp/sub	Thiosulfate Titrant (ml)	[ClO <sub>3</sub> ] (mM)	Reduction (%)
2	100	2	80	0.001	-1	1	-1	-1	-1	1	14.25	0.24	38.50
3	50	4	70	0.001	1	-1	1	-1	1	1	33.90	0.57	-4.59
4	50	4	80	0.01	1	1	-1	1	1	-1	2.20	0.04	93.69
5	100	4	70	0.01	-1	1	1	-1	-1	-1	20.25	0.34	12.61
7	50	4	70	0.01	-1	1	-1	-1	1	1	10.60	0.18	57.11
8	50	2	80	0.01	1	-1	-1	-1	1	-1	2.05	0.03	95.19
9	100	2	80	0.01	1	-1	1	-1	-1	1	3.15	0.05	86.41
10	100	2	70	0.001	1	1	-1	1	-1	-1	28.30	0.47	-22.13
11	50	4	80	0.001	-1	-1	1	1	1	-1	15.30	0.26	28.55
12	50	2	80	0.001	-1	1	1	-1	1	-1	11.40	0.19	34.25
13	100	4	80	0.001	-1	-1	-1	1	-1	1	15.43	0.26	33.41
15	100	2	70	0.01	-1	-1	1	1	-1	-1	16.50	0.28	28.79
16	50	2	70	0.01	-1	-1	-1	1	1	1	15.18	0.25	77.49
17	100	4	70	0.001	1	-1	-1	-1	-1	-1	28.20	0.47	-21.70
18	50	2	70	0.001	1	1	1	1	1	1	33.40	0.56	15.00
19	100	4	80	0.01	1	1	1	1	-1	1	7.05	0.12	69.58

# FINAL RESULTS AND FACTORIAL ANALYSIS OF EXPERIMENTAL PROGRAM 1

## CALCULATION OF MAIN AND INTERACTION EFFECTS

### MAIN EFFECTS

Parameter	[ClO <sub>3</sub> ] (mM)	Reduction %
Substitution		
sigma +	2.22	225.48
sigma -	2.07	396.69
difference	0.15	-171.21
effect	0.02	-21.40
pH		
sigma +	2.22	268.66
sigma -	2.07	353.51
difference	0.15	-84.85
effect	0.02	-10.61
Temperature		
sigma +	1.18	479.58
sigma -	3.11	142.60
difference	-1.93	336.98
effect	-0.24	42.12
Catalyst		
sigma +	1.28	520.87
sigma -	3.00	101.31
difference	-1.72	419.56
effect	-0.22	52.45

### INTERACTION EFFECTS

Parameter	[ClO <sub>3</sub> ] (mM)	Reduction %
temp/cat		
sigma +	2.30	311.45
sigma -	1.98	310.72
difference	0.32	0.73
effect	0.04	0.09
pH/cat		
sigma +	2.12	298.61
sigma -	2.16	323.56
difference	-0.04	-24.95
effect	0.00	-3.12
sub/cat		
sigma +	2.35	270.60
sigma -	1.94	351.57
difference	0.41	-80.97
effect	0.05	-10.12
pH/temp		
sigma +	2.22	324.39
sigma -	2.06	297.78
difference	0.16	26.62
effect	0.02	3.33

Parameter	[ClO <sub>3</sub> ] (mM)	Reduction %
pH/sub		
sigma +	2.07	396.69
sigma -	2.22	225.48
difference	-0.15	171.21
effect	-0.02	21.40
temp/sub		
sigma +	2.22	372.91
sigma -	2.07	249.26
difference	0.15	123.65
effect	0.02	15.46

CONFIDENCE INTERVAL CALCULATION USING CENTRE POINT

Run Number	Substitution	[ClO <sub>2</sub> ] (mM)	Reduction (%)
1	75	0.34	65.8523768
6	75	0.34	65.43
14	75	0.33	66.86
20	75	0.36	63.78
Average		0.34	65.48
Standard deviation		0.0154335	1.55
95% confidence interval		0.0332053	3.33

CURVATURE CALCULATION

	[ClO <sub>2</sub> ] (mM)	Reduction (%)
Average of all runs	0.27	38.89
Centre point average	0.3416667	65.48
Difference	-0.073792	-26.59
Confidence interval	0.0417824	4.18



SUMMARY OF RESULTS FOR EXPERIMENTAL PROGRAM 2

Variable	Chlorate Residual (mmol)	% ClO <sub>2</sub> Charge	Chlorate concentration Reduction (%)	Kappa	Kappa Decrease	Brightness (%)	Brightness Gain (%)	Viscosity (cps)	Viscosity Loss (cps)
95% Confidence Interval	0.0145	0.352	1.581	0.541	0.541	0.549	0.549	0.1999	0.2
Main Effects									
Time	-0.071	-5.52	36.98	0.0125	-0.0125	-0.418	-0.418	-1.399	1.399
Temperature	-0.0252	-4.59	26.02	-0.0875	0.188	-0.498	0.9	-1.869	0.754
Substitution	-0.00085	-5.148	-11.99	-1.013	0.513	-2.885	-0.48	2.234	-1.699
Catalyst Concentration	-0.0146	-5.482	37.82	0.038	-0.04	1.173	1.17	-0.249	0.25
Interaction Effects									
Temperature/Time	-0.003	0.621	-3.58	0.213	-0.213	-0.753	-0.753	-0.239	0.239
Substitution/Time	-0.00085	1.972	5.47	-0.163	0.163	-0.415	-0.415	-0.541	0.541
Catalyst/Time	-0.0388	2.231	-15.76	-0.113	0.113	0.1125	0.818	-0.399	0.399
Substitution/Temperature	-0.0098	2.842	-3.206	0.875	0.413	0.4125	-0.82	-0.431	0.336
Substitution/Catalyst	-0.0138	1.642	7.849	0.2625	-0.263	-0.2625	0.165	0.179	-0.179
Catalyst/Temperature	-0.00981	-0.0744	4.913	-0.0125	0.013	0.5875	0.588	0.11125	-0.111
Overall Curvature									
Curvature	0.064	2.423	-25.5	0.652	0.1	0.323	-1.28	-1.114	-0.269
confidence interval	0.013	0.443	1.99	0.681	0.68	0.691	0.691	0.25	0.252

CALCULATION OF CONFIDENCE INTERVAL USING CENTRE POINT RESULTS

Run Number	[ClO <sub>3</sub> ] (mM)	[ClO <sub>3</sub> ] Reduction (%)	Kappa Number (ml Thio)	Kappa Reduction (ml Thio)	Brightness (%)	Brightness Gain (%)	Viscosity (cps)	Viscosity Loss (cps)
1	0.188	79.455	6.900	-0.400	48.010	1.490	20.620	2.030
9	0.175	80.909	6.600	-0.100	47.620	1.100	20.570	2.080
19	0.183	80.000	6.400	0.100	47.240	0.720	20.750	1.900
Average	0.182	80.121	6.633	-0.133	47.623	1.103	20.647	2.003
Standard deviation	0.007	0.735	0.252	-0.252	0.385	0.385	0.093	0.093
95% confidence interval	0.014	1.581	0.541	0.541	0.828	0.828	0.200	0.200

CALCULATION OF OVERALL CURVATURE USING OVERALL AVERAGE AND CENTRE POINT VALUES

Run Number	[ClO <sub>3</sub> ] (mM)	[ClO <sub>3</sub> ] Reduction (%)	Kappa Number (ml Thio)	Kappa Reduction (ml Thio)	Brightness (%)	Brightness Gain (%)	Viscosity (cps)	Viscosity Loss (cps)
Average	0.247	54.62	5.98	-0.23	48.23	0.11	19.53	1.73
Centre point	0.182	80.12	6.63	-0.13	47.62	1.10	20.65	2.00
Curvature	0.064	-25.50	-0.65	0.10	0.61	-0.99	-1.11	-0.27
95% confidence interval	0.018	1.99	0.68	0.68	1.04	1.04	0.25	0.25

UNCATALYZED BLEACHING RUNS

Substitution (% eq. Cl <sub>2</sub> )	Catalyst Charge (wt. %)	Temp. (°C)	Time (hr)	Volume of Thiosulfate (ml)	[ClO <sub>3</sub> ] (mM)	Kappa Number (ml Thio)	Brightness (%)	Viscosity (cps)
50	0	80	2	37.95	0.633	5.80	45.54	20.49
50	0	70	2	40.05	0.668	6.20	47.34	21.51
50	0	40	2	40.95	0.683	6.10	47.98	22.21
75	0	75	2	55	0.917	6.5	46.52	22.65
100	0	80	2	28.05	0.468	5.80	49.31	21.93
100	0	70	2	27.00	0.450	5.20	50.30	23.01
100	0	40	2	27.80	0.463	5.60	54.26	23.75

CENTRE POINT RUNS

Run Number	Substitution (% eq. Cl <sub>2</sub> )	Catalyst Charge (wt. %)	Temp. (°C)	Time (hr)	Volume of Thiosulfate (ml)	[ClO <sub>3</sub> ] (mM)	Kappa Number (ml Thio)	Brightness (%)	Viscosity (cps)
1	75	0.01	75	3	10.80	0.180	6.90	48.01	20.62
9	75	0.01	75	3	10.50	0.175	6.60	47.62	20.10
19	75	0.01	75	3	11.00	0.183	6.40	47.24	20.50

FACTORIAL ANALYSIS OF EXPERIMENTAL PROGRAM 2

RESULTS SUMMARIZED WITH RESPECT TO MAIN EFFECTS

Run Number	Substitution (% eq. Cl <sub>2</sub> )	Catalyst Charge (wt. %)	Temp. (°C)	Time (hr)	Substitution (% eq. Cl <sub>2</sub> )	Catalyst Charge (wt. %)	Temp. (°C)	Time (hr)	Volume of Thiosulfate (ml)	[ClO <sub>3</sub> ] (mM)	[ClO <sub>3</sub> ] Reduction (%)
2	100	0.005	80	4	1	-1	1	1	9.30	0.155	66.84
3	100	0.015	70	2	1	1	-1	-1	18.20	0.303	32.59
4	50	0.005	80	2	-1	-1	1	-1	23.40	0.390	38.34
5	100	0.005	70	2	1	-1	-1	-1	28.20	0.470	-4.44
6	50	0.015	80	4	-1	1	1	1	2.70	0.045	92.89
7	50	0.005	70	2	-1	-1	-1	-1	36.30	0.605	9.36
8	100	0.005	80	2	1	-1	1	-1	29.70	0.495	-5.88
10	100	0.015	80	4	1	1	1	1	2.29	0.038	91.84
11	50	0.015	70	2	-1	1	-1	-1	20.90	0.348	47.82
12	50	0.015	70	4	-1	1	-1	1	8.90	0.148	77.78
13	100	0.015	80	2	1	1	1	-1	3.55	0.059	87.34
14	100	0.005	70	4	1	-1	-1	1	14.40	0.240	46.67
15	50	0.005	70	4	-1	-1	-1	1	20.40	0.340	49.06
16	50	0.005	80	4	-1	-1	1	1	5.40	0.090	85.77
17	100	0.015	70	4	1	1	-1	1	7.00	0.117	74.07
18	50	0.015	80	2	-1	1	1	-1	6.10	0.102	83.93

RESULTS SUMMARIZED WITH RESPECT TO MAIN EFFECTS

Run Number	Substitution (% eq. Cl <sub>2</sub> )	Catalyst Charge (wt. %)	Temp. (°C)	Time (hr)	Substitution (% eq. Cl <sub>2</sub> )	Catalyst Charge (wt. %)	Temp. (°C)	Time (hr)	Kappa Number (ml Thio)	Kappa Reduction (ml Thio)	Brightness (%)	Brightness Gain (%)	Viscosity (cps)	Viscosity Loss (cps)
2	100	0.005	80	4	1	-1	1	1	5.30	0.50	47.29	-2.02	18.35	2.58
3	100	0.015	70	2	1	1	-1	-1	5.70	-0.50	50.07	-0.23	22.75	-0.61
4	50	0.005	80	2	-1	-1	1	-1	6.20	-0.40	46.47	0.93	18.05	2.44
5	100	0.005	70	2	1	-1	-1	-1	5.50	-0.30	50.13	-0.17	22.37	-0.23
6	50	0.015	80	4	-1	1	1	1	6.30	-0.50	47.59	2.05	16.77	3.72
7	50	0.005	70	2	-1	-1	-1	-1	6.70	-0.50	47.10	-0.24	19.65	1.86
8	100	0.005	80	2	1	-1	-1	-1	5.20	0.60	49.36	0.05	20.56	0.37
10	100	0.015	80	4	1	1	1	1	5.60	0.20	49.42	0.11	18.29	2.64
11	50	0.015	70	2	-1	1	-1	-1	6.60	-0.40	45.96	-1.38	19.42	2.09
12	50	0.015	70	4	-1	1	-1	1	6.50	-0.30	47.99	0.65	18.36	3.15
13	100	0.015	80	2	1	1	1	-1	5.80	0.00	50.81	1.50	20.80	0.13
14	100	0.005	70	4	1	-1	-1	1	5.30	-0.10	49.25	-1.05	21.46	0.68
15	50	0.005	70	4	-1	-1	-1	1	6.50	-0.30	46.28	-1.06	19.11	2.40
16	50	0.005	80	4	-1	-1	1	1	7.00	-1.20	45.30	-0.24	17.71	2.78
17	100	0.015	70	4	1	1	-1	1	5.40	-0.20	51.08	0.78	20.62	1.52
18	50	0.015	80	2	-1	1	1	-1	6.10	-0.30	47.64	2.10	18.26	2.23

# FACTORIAL ANALYSIS OF EXPERIMENTAL PROGRAM 2

RESULTS SUMMARIZED WITH RESPECT TO INTERACTION EFFECTS

Run Number	temp/time	sub/time	cat/time	sub/temp	sub/cat	cat/temp	[ClO <sub>3</sub> ] (mM)	[ClO <sub>3</sub> ] Reduction (%)	Kappa Number (ml Thio)	Kappa Reduction (ml Thio)	Brightness (%)	Brightness Gain (%)	Viscosity (cps)	Viscosity Loss (cps)
2	1	1	-1	1	-1	-1	0.155	66.84	5.30	0.50	47.29	-2.02	18.35	2.58
3	1	-1	-1	-1	1	-1	0.303	32.59	5.70	-0.50	50.07	-0.23	22.75	-0.61
4	-1	1	1	-1	1	-1	0.390	38.34	6.20	-0.40	46.47	0.93	18.05	2.44
5	1	-1	1	-1	-1	1	0.470	-4.44	5.50	-0.30	50.13	-0.17	22.37	-0.23
6	1	-1	1	-1	-1	1	0.045	92.89	6.30	-0.50	47.59	2.05	16.77	3.72
7	1	1	1	1	1	1	0.605	9.36	6.70	-0.50	47.10	-0.24	19.65	1.86
8	-1	-1	1	1	-1	-1	0.495	-5.88	5.20	0.60	49.36	0.05	20.56	0.37
10	1	1	1	1	1	1	0.038	91.84	5.60	0.20	49.42	0.11	18.29	2.64
11	1	1	-1	1	-1	-1	0.348	47.82	6.60	-0.40	45.96	-1.38	19.42	2.09
12	-1	-1	1	1	-1	-1	0.148	77.78	6.50	-0.30	47.99	0.65	18.36	3.15
13	-1	-1	-1	1	1	1	0.059	87.34	5.80	0.00	50.81	1.50	20.80	0.13
14	-1	1	-1	-1	-1	1	0.240	46.67	5.30	-0.10	49.25	-1.05	21.46	0.68
15	-1	-1	-1	1	1	1	0.340	49.06	6.50	-0.30	46.28	-1.06	19.11	2.40
16	1	-1	-1	-1	1	-1	0.090	85.77	7.00	-1.20	45.30	-0.24	17.71	2.78
17	-1	1	1	-1	1	-1	0.117	74.07	5.40	-0.20	51.08	0.78	20.62	1.52
18	-1	1	-1	-1	-1	1	0.102	83.93	6.10	-0.30	47.64	2.10	18.26	2.23

FACTORIAL ANALYSIS OF MAIN EFFECTS

Parameter	[ClO <sub>3</sub> ] (mM)	[ClO <sub>3</sub> ] Reduction (%)	Kappa Number (ml Thio)	Kappa Reduction (ml Thio)	Brightness (%)	Brightness Gain (%)	Viscosity (cps)	Viscosity Loss (cps)
Time								
sigma +	1.173	584.92	47.90	-1.90	384.20	-0.78	150.67	19.47
sigma -	1.740	289.05	47.80	-1.80	387.52	2.56	161.86	8.28
difference	-0.567	295.86	0.10	-0.10	-3.34	-3.34	-11.19	11.19
effect	-0.071	36.98	0.01	-0.01	-0.42	-0.42	-1.40	1.40
Temperature								
sigma +	1.374	541.06	47.50	-1.10	383.88	4.48	148.79	19.47
sigma -	1.576	332.91	48.20	-2.60	387.86	-2.70	163.74	8.28
difference	-0.202	208.16	-0.70	1.50	-3.98	7.18	-14.95	11.19
effect	-0.025	26.02	-0.09	0.19	-0.50	0.90	-1.87	1.40
Substitution								
sigma +	1.877	389.03	43.80	0.20	397.41	-1.03	165.20	19.47
sigma -	1.884	484.94	51.90	-3.90	374.33	2.81	147.33	8.28
difference	-0.007	-95.91	-8.10	4.10	23.08	-3.84	17.87	11.19
effect	-0.001	-11.99	-1.01	0.51	2.89	-0.48	2.23	1.40
Catalyst								
sigma +	1.161	588.25	48.00	-2.00	390.56	5.58	155.27	19.47
sigma -	1.278	285.72	47.70	-1.70	381.18	-3.80	157.26	8.28
difference	-0.117	302.53	0.30	-0.30	9.38	9.38	-1.99	11.19
effect	-0.015	37.82	0.04	-0.04	1.17	1.17	-0.25	1.40

FACTORIAL ANALYSIS OF INTERACTION EFFECTS

Interaction	[ClO <sub>2</sub> ] (mM)	[ClO <sub>2</sub> ] Reduction (%)	Kappa Number (ml Thio)	Kappa Reduction (ml Thio)	Brightness (%)	Brightness Gain (%)	Viscosity (cps)	Viscosity Loss (cps)
temp/time								
sigma +	2.055	422.66	48.70	-2.70	382.86	-2.12	155.31	19.47
sigma -	2.076	451.31	47.00	-1.00	388.88	3.90	157.22	8.28
difference	-0.021	-28.65	1.70	-1.70	-6.02	-6.02	-1.91	11.19
effect	-0.003	-3.58	0.21	-0.21	-0.75	-0.75	-0.24	1.40
sub/time								
sigma +	1.995	458.87	47.20	-1.20	384.21	-0.77	154.10	19.47
sigma -	2.002	415.11	48.50	-2.50	387.53	2.55	158.43	8.28
difference	-0.007	43.76	-1.30	1.30	-3.32	-3.32	-4.33	11.19
effect	-0.001	5.47	-0.16	0.16	-0.42	-0.42	-0.54	1.40
cat/time								
sigma +	2.308	373.95	47.40	-1.40	389.14	4.16	154.67	19.47
sigma -	2.618	500.02	48.30	-2.30	382.60	-2.38	157.86	8.28
difference	-0.310	-126.07	-0.90	0.90	6.54	6.54	-3.19	11.19
effect	-0.039	-15.76	-0.11	0.11	0.82	0.82	-0.40	1.40
sub/temp								
sigma +	2.189	424.16	48.20	-0.20	384.21	-2.39	154.54	19.47
sigma -	2.268	449.81	47.50	-3.50	387.53	4.17	157.99	8.28
difference	-0.079	-25.65	0.70	3.30	-3.32	-6.56	-3.45	11.19
effect	-0.010	-3.21	0.09	0.41	-0.41	-0.82	-0.43	1.40
sub/cat								
sigma +	1.942	468.38	48.90	-2.90	386.53	1.55	156.98	19.47
sigma -	2.053	405.59	46.80	-0.80	385.21	0.23	155.55	8.28
difference	-0.110	62.79	2.10	-2.10	1.32	1.32	1.43	11.19
effect	-0.014	7.85	0.26	-0.26	0.16	0.17	0.18	1.40
cat/temp								
sigma +	1.899	456.64	47.80	-1.80	388.22	3.24	156.71	19.47
sigma -	1.978	417.33	47.90	-1.90	383.52	-1.46	155.82	8.28
difference	-0.079	39.31	-0.10	0.10	4.70	4.70	0.89	11.19
effect	-0.010	4.91	-0.01	0.01	0.59	0.59	0.11	1.40



PHYSICAL TESTING RESULTS FOR THE RUNS AT 80 °C

Run Number	2	4	6	8	10	13	16	18
Factor Settings								
Time (hr)	4	2	4	2	4	2	4	2
Substitution (% eq. Cl <sup>2</sup> )	100	50	50	100	100	100	50	50
Catalyst Charge (wt. %)	0.005	0.005	0.015	0.005	0.015	0.015	0.005	0.015
Parameter								
Tesile Index (N.m/g)	28.90	30.26	29.11	32.40	31.72	29.80	30.16	32.60
Breaking length (km)	2.95	3.09	2.97	3.30	3.23	3.04	3.08	3.33
Tear Index (mN.m <sup>2</sup> /g, 1-ply)	15.60	15.57	15.23	14.96	15.33	15.15	16.45	15.35
Tear strength (mN, 1 ply)	936.24	934.36	913.74	897.83	919.99	908.94	987.18	921.25
Burst Index (kPa.m <sup>2</sup> /g)	2.20	2.27	1.93	2.05	2.25	2.05	2.36	2.26
Burst strength (KPa)	130.87	135.63	120.61	127.43	136.69	126.08	130.50	136.70
Zero Span Index (km)	13.94	14.23	13.01	14.17	13.67	14.45	13.79	13.99
Bulk (cm <sup>3</sup> /g)	1.88	1.98	1.91	1.93	1.88	1.99	2.06	1.95
Opacity	94.94	94.94	94.94	94.94	93.27	94.94	93.52	94.94

# FACTORIAL ANALYSIS OF THE RUNS AT 80 °C

Parameter	Time				Substitution				Catalyst Charge			
	sigma +	sigma -	difference	effect	sigma +	sigma -	difference	effect	sigma +	sigma -	difference	effect
Tesile Index (N m/g)	119.89	125.06	-5.17	-1.29	122.82	122.12	0.70	0.17	123.23	121.72	1.51	0.38
Breaking length (km)	12.23	12.76	-0.53	-0.13	12.53	12.46	0.07	0.02	12.57	12.41	0.15	0.04
Tear Index (mN.m <sup>2</sup> /g, 1-ply)	62.62	61.04	1.58	0.39	61.05	62.61	-1.56	-0.39	61.07	62.59	-1.53	-0.38
Tear strength (mN, 1 ply)	3757.16	3662.38	94.78	23.70	3663.01	3756.53	-93.53	-23.38	3663.93	3755.61	-91.68	-22.92
Burst Index (kPa.m <sup>2</sup> /g)	8.74	8.63	0.11	0.03	8.55	8.82	-0.27	-0.07	8.50	8.88	-0.38	-0.09
Burst strength (kPa)	518.68	525.85	-7.17	-1.79	521.07	523.45	-2.38	-0.59	520.08	524.44	-4.36	-1.09
Zero Span Index (km)	54.41	56.84	-2.43	-0.61	56.23	55.02	1.21	0.30	55.12	56.13	-1.00	-0.25
Bulk (cm <sup>3</sup> /g)	7.73	7.84	-0.11	-0.03	7.68	7.89	-0.22	-0.05	7.72	7.85	-0.12	-0.03
Opacity (%)	376.67	379.76	-3.09	-0.77	378.09	378.34	-0.25	-0.06	378.09	378.34	-0.25	-0.06

CALCULATION OF THE 95% CONFIDENCE INTERVAL USING THE CENTREPOINT RUNS

Parameter	Run Number			Standard Deviation	95% Confidence Interval	Standard Deviation	95% Confidence Interval
	1	9	13				
				Runs at 80°C			
				Uncatalyzed and Catalyzed Runs			
Tesile Index (N.m/g)	31.65	30.77	32.92	1.08	3.28	1.08	4.64
Breaking length (km)	3.23	3.14	3.36	0.11	0.34	0.11	0.48
Tear Index (mN.m <sup>2</sup> /g, 1-ply)	15.70	15.41	15.66	0.16	0.49	0.16	0.69
Tear strength (mN, 1 ply)	942.15	924.47	939.65	9.57	29.10	9.57	41.16
Burst Index (kPa.m <sup>2</sup> /g)	2.26	2.56	2.28	0.17	0.51	0.17	0.72
Burst strength (KPa)	136.78	135.11	138.60	1.75	5.31	1.75	7.51
Zero Span Index (km)	13.94	14.35	14.61	0.34	1.04	0.34	1.46
Bulk (cm <sup>3</sup> /g)	1.95	2.08	1.88	0.11	0.32	0.11	0.46
Opacity (%)	94.94	93.24	94.12	0.85	2.59	0.85	3.66

FACTORIAL COMPARISON OF THE UNCATALYZED RUNS AT 40°C AND THE CATALYZED RUNS AT 80°C

Temperature (°C)	Temperature Effect				Substitution Effect			
	40		80		40		80	
	Substitution (% eq. Cl <sub>2</sub> )	0	100	50	100	0	100	50
Catalyst Charge (wt. %)								
Parameter								
Parameter	40		80		80		0.015	
	sigma +	sigma -	difference	effect	sigma +	sigma -	difference	effect
Tesile Index (N.m/g)	31.54	32.16	29.11	31.72	60.83	63.70	-2.88	-1.44
Breaking length (km)	3.22	3.28	2.97	3.23	6.20	6.50	-0.29	-0.15
Tear Index (mN.m <sup>2</sup> /g. 1-ply)	15.29	15.64	15.23	15.33	30.56	30.94	-0.37	-0.19
Tear strength (mN. 1 ply)	917.60	938.63	913.74	919.99	1833.74	1856.23	-22.50	-11.25
Burst Index (kPa.m <sup>2</sup> /g)	2.23	2.10	1.93	2.25	4.19	4.33	-0.15	-0.07
Burst strength (KPa)	133.82	126.24	120.61	136.69	257.30	260.05	-2.75	-1.38
Zero Span Index (km)	14.25	14.71	13.01	13.67	26.68	28.96	-2.28	-1.14
Bulk (cm <sup>3</sup> /g)	1.92	2.04	1.91	1.88	3.79	3.96	-0.17	-0.09
Opacity	93.30	90.94	94.94	93.27	188.21	184.24	3.97	1.98

Temperature (°C)	Catalyst Charge Effect			
	40		80	
	Substitution (% eq. Cl <sub>2</sub> )	0	100	50
Catalyst Charge (wt. %)				
Parameter				
Parameter	40		80	
	sigma +	sigma -	difference	effect
Tesile Index (N.m/g)	31.54	32.16	29.11	31.72
Breaking length (km)	3.22	3.28	2.97	3.23
Tear Index (mN.m <sup>2</sup> /g. 1-ply)	15.29	15.64	15.23	15.33
Tear strength (mN. 1 ply)	917.60	938.63	913.74	919.99
Burst Index (kPa.m <sup>2</sup> /g)	2.23	2.10	1.93	2.25
Burst strength (KPa)	133.82	126.24	120.61	136.69
Zero Span Index (km)	14.25	14.71	13.01	13.67
Bulk (cm <sup>3</sup> /g)	1.92	2.04	1.91	1.88
Opacity	93.30	90.94	94.94	93.27