



Sodium dichromate from Montana chrome ore
by David E Heath

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering
Montana State University
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Abstract:

In 1956 Mouat Industries at Columbus, Montana constructed a pilot plant for the production of sodium dichromate using chrome ore from the Stillwater complex in southwestern Montana. This project at Montana State College was initiated to aid in the development of this pilot plant.

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Conversions of chromic oxide increased with an increase in the per cent sodium carbonate, with an increase in the diluent to concentrates ratio and with an increase in the roasting temperature. The addition of recycle lowered the per cent conversion. For mixtures containing high proportions of limestone, a change in the amount of limestone affected the conversion only by diluting the mixture (changing the actual amount of Na_2CO_3 to Cr_2O_3). There does, however, appear to be a point at lower proportions of limestone where a decrease in the amount of limestone causes a very sharp decrease in per cent conversion.

The per cent conversion obtained for mixtures utilizing limestone are much higher than for mixtures not containing a calcium compound. This increase is due in part to an increase in the sodium carbonate to chromic oxide ratio and in part to a decrease in the recycle to concentrates ratio. It is also partly due to an increase in the ratio of limestone to concentrates.

The amount of Cr_2O_3 converted per 100 pounds of charge was increased with an increase in temperature and an increase in the weight per cent sodium carbonate. However, a decrease in the diluent to concentrates ratio increased the amount of Cr_2O_3 converted per 100 pounds of charge.

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FROM

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ABSTRACT

In 1956 Mouat Industries at Columbus, Montana constructed a pilot plant for the production of sodium dichromate using chrome ore from the Stillwater complex in southwestern Montana. This project at Montana State College was initiated to aid in the development of this pilot plant.

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INTRODUCTION

Statement of Problem

Chrome ore may be utilized in three main areas: for metallurgical purposes (chromium alloys), in the production of chrome chemicals and related products, and in the manufacture of refractories. At present, nearly all chrome ore used in the United States is imported from South Africa. There are, however, chrome deposits of possible commercial interest in Washington, California, Montana, Oregon, and Alaska. Considerable interest has been given to the utilization of domestic chrome ore although it is of a lower grade than South African ore.

In 1956, Mouat Industries constructed a pilot plant at Columbus, Montana for the production of sodium dichromate, a basic chrome chemical. The pilot plant utilizes chrome ore from the Stillwater complex in southwestern Montana.

This project at Montana State College was initiated to aid in the development of the pilot plant at Columbus and thereby increase the utilization of Montana's natural resources.

There are very few companies in the United States that are major producers of chromates and the technical details of the processes are not revealed. General information concerning dichromate production is contained in the literature; however, this information differs from source to source.

Present Practice

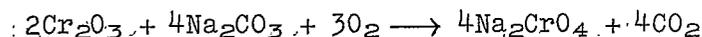
There are five basic steps in the production of sodium dichromate: (1) preparing kiln feed; (2) roasting; (3) leaching; (4) purifying; and (5) concentrating.

The basic ingredients of the kiln feed are sodium carbonate and chrome ore. Other constituents may also be included in the mixture. Udy (6) states that an inert diluent such as recycle residue may be included to lower the proportion of soda ash. He also states that either burned lime or hydrated lime may be used in the mixture and that limestone is not generally satisfactory. On the other hand, Shreve (5) gives a mixture containing limestone but neglects to mention the use of recycle.

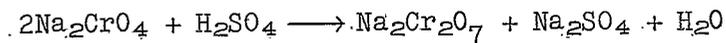
After the desired kiln feed has been prepared, it is fed to a rotary kiln and is roasted at 1900 to 2200°F. In the early 1900's a reverberatory furnace was used in the production of sodium dichromate; however, now the use of rotary kilns is standard in America. The rotary kiln is limited to the handling of mixtures that do not become excessively sticky. Since sodium carbonate is liquid at the roasting temperature, an excessive amount of sodium carbonate will cause the mixture to become sticky and the material will adhere to the kiln wall. This results in the discharge of unreacted balls or lumps. Udy (6) states that for this reason the amount of sodium carbonate in this mixture is limited to about 18 to 22 per cent. On this point there is some disagreement. Shreve (5)

describes a mixture containing about 24 per cent sodium carbonate.

While in the kiln, sodium carbonate reacts with the chromic oxide in the ore producing soluble sodium chromate. The reaction which yields the chromate is:



This soluble sodium chromate is leached from the residue. Generally leaching is done in a battery of leaching boxes. Liquid is pumped onto the top of the material in the box and then it percolates downward and is drawn off as a clear solution. The clear solution contains dissolved aluminum which is precipitated by adding sulfuric acid until the solution has a pH of 9. The precipitated alumina is filtered leaving a solution containing essentially pure sodium chromate. This solution is again treated with sulfuric acid to convert the chromate to dichromate according to the reaction:



Part of the sodium sulfate comes out of solution at this point and the remainder separates upon concentration and cooling. After precipitation, the sodium sulfate is separated from the dichromate solution by means of a centrifuge. The dichromate solution is then evaporated further to a specific gravity of 1.68 and final pH adjustments are made.

The finished product is an aqueous solution of sodium dichromate having a specific gravity of 1.68 and a pH of 4.7 to 5.1 and it is marketed in this form.

Scope of This Investigation

Although the Mouat Industries' plant at Columbus, Montana is operated quite similarly to the above procedure, there are some differences. The first difference is that Mouat Industries utilize domestic chrome ore rather than imported ore. Since the domestic ore is of a low grade, it must be concentrated to obtain a material containing from 32 to 38 weight per cent Cr_2O_3 . This concentrating is accomplished by passing the ore over a wet table which separates the ore by means of difference in specific gravity.

Secondly, when the kiln feed is prepared at Columbus, the components are mixed together in water. The mixture is then dried and fed to the kiln. The justification for this wet mix seems to be that if the sodium carbonate is dissolved and then redeposited upon the insoluble components, there will be uniform distribution of sodium carbonate on chrome ore.

Until recently, a third difference between the procedure at Columbus and the procedure stated in the literature was that no calcium compound was used in the kiln feed at Columbus. In earlier work at Montana State College, Gore (2) investigated the effects of retention time, temperature, sodium carbonate, and recycle to concentrates ratio upon conversion when no calcium was used. The highest conversion of Cr_2O_3 to soluble

chromates for that study was 42.2 per cent. Since the completion of Gore's study, Mouat Industries have been using lime in their kiln feed mixture. This has increased the conversion of Cr_2O_3 to the seventy per cent range. Still, however, nothing is known about how a change in the amount of calcium affects the per cent conversion or if the cheaper limestone may be used in place of lime.

Yet another difference between Mouat's procedure and the procedure given in the literature is in the leaching step. The literature describes a set of counter-current leach boxes. Mouat uses a ^{single} ~~single~~ leach tank in which water and kiln discharge are mixed. This slurry is pumped to an acid addition tank where some sulfuric acid is added and then the slurry is filtered on an Oliver Filter.

In order to have an economically sound operation, one must obtain a high per cent conversion to soluble chrome. This is especially true when working with domestic ores which must be concentrated to obtain a material rich in chromic oxide. After this high conversion is obtained one ^{MUST} ~~must~~ recover as much of the soluble chromate as possible. Hence the factors affecting conversion in the roasting step and the type of leaching which will recover a maximum amount of soluble chromate are important.

In this investigation only factors affecting conversions such as sodium carbonate, limestone, temperature, and recycle were investigated.

EQUIPMENT, RAW MATERIAL, AND PROCEDURE

Raw Material

The feeds blended for this study consisted of four ingredients in varied proportions: chrome ore concentrates, sodium carbonate, recycle material, and calcium carbonate.

The chrome ore concentrates used were from the Benbow mine, Stillwater County, Montana. A complete analysis of the concentrates used in this study was not available; however, a typical analysis of concentrates obtained from the Stillwater complex is listed below.

Fe	16.35%	MgO	15.80%
Al ₂ O ₃	15.82%	Cr ₂ O ₃	38.50%
SiO ₂	6.88%	CaO	0.20%

The above analysis was obtained from Dr. Dwight Harris of the American Chrome Company at Nye, Montana. It is an analysis of a monthly composite of concentrates being produced by American Chrome Company under Government contract. The chrome ore concentrates used in this study were analyzed for chromium content and were found to contain 38.0 per cent Cr₂O₃.

The sodium carbonate and recycle material as well as the concentrates were obtained from the Mouat Industries at Columbus. The recycle material is the residue from the leached kiln product produced by the Columbus plant. The recycle material used for this study contained 12.7 per cent unreacted Cr₂O₃. The sodium carbonate is that used in the

Columbus plant and is produced by Intermountain Chemical Company Division of the FMC Corporation at Green River, Wyoming.

The calcium carbonate was donated by the Elliston Lime Company of Helena, Montana. Mr. A. Leo Gallagher, manager of the Elliston Lime Company, indicates that their limestone contains 98.7 per cent CaCO_3 and from 0.5 to 0.8 per cent acid insolubles.

Feed Preparation

Both the chrome ore concentrates and the calcium carbonate were crushed in a ball mill to obtain a material of 100 per cent minus 200 mesh.

The recycle material contained a considerable amount of soluble sodium chromate along with some unreacted sodium carbonate. Hence, it was washed and filtered until no trace of yellow chromate could be detected. The wet recycle material was dried and then ball-milled to produce a fine powder.

A weighed amount of sodium carbonate was added to a large beaker of water and these components were stirred until the sodium carbonate was completely dissolved. After complete solution of the sodium carbonate, proper amounts of chrome ore concentrates, calcium carbonate, and recycle material (when used) were added to the beaker. The resulting mixture was boiled and stirred until a thick mass was obtained. This mass was then dried, ball milled, and screened to obtain a minus 200 mesh fraction. This fraction was used in the roasting step.

Muffle Design and Operation

A Model 1220 Denver Fire Clay Company muffle furnace was used for all runs. The necessary oxidizing atmosphere was obtained by introducing air through a 3/4-in. diameter quartz tube placed through an aperture in the muffle door. The temperature was controlled manually by adjusting the gas line valve and burner air valve. A Brown Instrument potentiometer in conjunction with a Chromel-Alumel thermocouple probe was used to read temperatures. It was possible to control the temperature inside the muffle to within ten Fahrenheit degrees.

The samples were placed on brick pallets in the cold muffle furnace and allowed to warm up to the desired temperature. The air supply was then turned on and retention times measured from this point. All samples were left in the furnace at the desired temperature for 60 minutes.

Treatment of Samples

The roasted samples were ground in a small ceramic ball mill. These samples were then analyzed in duplicate for both soluble and total chrome.

A sodium peroxide (Na_2O_2) fusion was employed for total chrome analysis. Approximately five grams of Na_2O_2 were added to 0.500 grams of sample in an Armco iron crucible. The bulk of the Na_2O_2 was thoroughly mixed with the sample and the remaining Na_2O_2 was used to completely cover the top of the sample. The fusion was performed in an electric furnace at 750°F for two hours. The fused sample was placed in a beaker

of distilled water and the crucible was washed free of fusion products. The sample was then boiled for fifteen minutes to destroy excess Na_2O_2 . After cooling, the sample was treated as described under "Chemical Treatment of Dissolved Samples" and titrated to determine total chrome.

A 1.000 gram sample was taken for soluble chrome analysis. This sample was placed on a filter paper and was washed with hot water to remove all the soluble chromate. This sample was then treated the same as the total chrome sample according to the following description.

Chemical Treatment of Dissolved Chromium Samples

1. Neutralize with 1:1 H_2SO_4 and dilute to 300 ml with distilled water.
2. Acidify with 60 ml of 1:1 H_2SO_4 and boil 15 min.
3. Add 10 ml of 2.5 per cent AgNO_3 solution. Add 5.0 grams of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (ammonium persulfate). Add 4.0 ml of 0.1 normal KMnO_4 (potassium permanganate). Boil 10 min.
4. Add 10 ml of 10 per cent NaCl solution. Boil 10 min.
5. Cool to room temperature and titrate.

Titration of Chromium Samples

1. Add 0.198 normal $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (ferrous ammonium sulphate) until the yellow solution changes through olive green to grass green. Then add 5 ml in excess.
2. Allow the solution to stand at least 5 minutes, then add 2 or 3 ml of 85 per cent phosphoric acid to sharpen the end point.
3. Back titrate with 0.198 normal KMnO_4 solution until a pink hue is observed.

The following calculation for per cent Cr_2O_3 is based on a 0.500 gram sample and titration solutions of 0.198 normal:

$$\begin{array}{r} \text{ml of 0.198 N. FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O} \\ \text{minus} \\ \text{ml of 0.198 N. KMnO}_4 \text{ equals per cent } \text{Cr}_2\text{O}_3. \end{array}$$

The per cent Cr_2O_3 must be divided by two for the 1.000 gm soluble chrome samples. If the standard solutions are not exactly 0.198 normal, the milliliters of solutions used must be adjusted to equivalents of 0.198 normal solutions before using the above expression for per cent Cr_2O_3 .

Standard Solutions

The potassium permanganate solution for titration was standardized with sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$). The ferrous ammonium sulphate was then standardized against the potassium permanganate solution.

In order to prevent oxidation of the ferrous ammonium sulphate by oxygen from the air, it was stored under an atmosphere of nitrogen. The details of standardizing as well as reagent preparation may be found in Scott's STANDARD METHODS OF ANALYSIS, VOLUME I. (4).

RESULTS.

Presentation of Results

This study was designed to evaluate the effects of various factors upon the conversion of chromic oxide in chrome ore concentrates to soluble sodium chromate. Factors studied were: weight per cent sodium carbonate in the roast mixture; temperature of roasting; and the amount and composition of diluent in the mixture. For this investigation the diluent was either crushed limestone or a combination of limestone and recycle residue. Half of the runs were made without recycle residue and half were completed with recycle residue. The four factors and the levels at which they were investigated are shown below.

	Level		
Factor	1	2	3
A	20	22	24
B	1900	2200	--
C	1	2	--
D	0.0	0.5	--

Where: Factor A is weight per cent sodium carbonate
Factor B is temperature in degrees Fahrenheit
Factor C is the ratio of lbs of diluent per lb
of concentrates
Factor D is weight fraction of diluent which
was recycle

Since each level of each factor listed above was investigated at each level of all other factors, this represents 24 runs. The results of these runs are listed in Table I on page 29.

Statistical Analysis of Results

The analysis of variance of the data for this experiment is presented in Table II on page 30. An analysis of variance permits the experimenter to determine at a known level of probability which of the variables affect the observations (in this case, which variables affect the conversion of chromic oxide to sodium chromate). The effect of a variable is said to be statistically significant if the variance ratio (F ratio) exceeds the specified value called the critical variance ratio. The variance ratio is obtained by dividing the mean square for the particular factor by the mean square for error. All the main effects were found to be significant at the one per cent level. When a factorial effect is significant at the one per cent level, the probability that the effect is actually not significant is 0.01.

For this experiment only four of the interactions were considered in the analysis of variance. The interactions considered are AD, BC, BD, and CD. The remaining interactions were assumed to have zero effect upon the response. Of the interactions investigated, AB and BD were found to be significant at the one per cent level while BC and CD were not significant. Details of the calculations for the analysis of variance may be found in texts such as Davies (1) or Ostle (3).

Means for each level of factors A, B, C, and D are shown in Tables IV, V, VI, and VII. The means in these tables are the mean values of all observations at one level of a specific factor. Two-way tables of

means for factors A and D and for factors B and D are presented in Tables VIII and IX. These two-way tables are obtained by summing the observations on two factors over the levels of the remaining two factors, and dividing by the number of observations on two factors over the levels of the remaining two factors, and dividing by the number of observations in each sum.

The estimated standard error of a mean is also given for each of the above tables. This value is obtained by dividing the error variance (error mean square) by the number of observations for each mean and taking the square root of this quotient.

By noting the above listed tables of means for the various levels of factors A, B, and C, it is observed that the mean increases with an increase in the level of these factors. However, the mean value of the response decreases as the level of factor D is increased. The two-way tables of means indicate that for the higher levels of factors A and B an increase in the level of D does not decrease the mean response as much as at the lower levels of factors A and B.

Discussion of Results

The data shown in Table I are plotted in Figures 1 and 2 and in Figures 3 and 4.

Figure 1 on page 34 is a plot of per cent conversion vs. weight per cent sodium carbonate for mixtures containing only limestone as diluent.

This plot shows an increase in per cent conversion with an increase in weight per cent sodium carbonate, with an increase in the temperature, and with an increase in the diluent to concentrates ratio.

Figure 2 on page 35 is a plot of per cent conversion vs. weight per cent sodium carbonate for mixtures containing a diluent composed of 50 per cent limestone and 50 per cent recycle material. This plot also shows an increase in conversion with an increase in weight per cent sodium carbonate, with an increase in the temperature, and with an increase in the diluent to concentrates ratio.

Figures 3 and 4 on pages 36 and 37 are plots of per cent conversion vs. weight per cent sodium carbonate for mixtures roasted at 1900°F and 2200°F, respectively.

One may observe from Figures 3 and 4 the difference in conversion obtained from mixtures containing 100 per cent limestone as a diluent and those containing a diluent of 50 per cent limestone and 50 per cent recycle. For a given weight per cent sodium carbonate in the charge and for a given temperature, mixtures containing a diluent of recycle and limestone yield lower conversions than mixtures containing a diluent composed of limestone alone. As the per cent sodium carbonate increases, the difference in conversion between mixtures containing recycle and those containing no recycle decreases. By noting both Figures 3 and 4 it is also observed that the difference in conversion between mixtures not containing recycle and those containing recycle is lowered by increasing

the temperature.

These four figures then show that conversions are increased by increasing the roasting temperature, by increasing the weight per cent sodium carbonate and by increasing the diluent to concentrates ratio. They also show that conversion is decreased by substituting recycle for limestone in the diluent. These results are also shown in the statistical analysis and may be observed by noting the tables of means shown on pages 31 and 32.

The data of Table I are plotted in Figures 5 and 6 as per cent conversion vs. pounds of sodium carbonate per pound of chromic oxide. Figure 5 on page 38 shows the results for mixtures roasted at 1900°F while Figure 6 on page 39 shows the results for feeds roasted at 2200°F. It may be observed from these plots that for mixtures containing only limestone as a diluent, the per cent conversion increases linearly with an increase in the sodium carbonate to chromic oxide ratio. This indicates that increasing the diluent to concentrates ratio (in this case the limestone to concentrates ratio) from 1 to 2 increases the conversion only because it increases the ratio of sodium carbonate to chromic oxide.

In Figures 5 and 6 there are three points labeled 1, 2, and 3, which all have a ratio of sodium carbonate to chromic oxide of approximately 1.44. These points do not, however, show the same per cent conversion. Point 1 in both Figures 5 and 6 represents the same mixture. The difference between point 1 in Figures 5 and 6 is the roasting temperature.

The same is true for points 2 and 3.

Since all of these points contain approximately the same ratio of sodium carbonate to chromic oxide but yield different per cent conversions, there is a question as to what causes the change in per cent conversion. There are two quantities that change from point 1 to point 2 and from point 2 to point 3. These quantities are the limestone to concentrates ratio and the recycle to concentrates ratio. The ratio of limestone to concentrates for the mixture giving point 1 on both figures is 1.0; for the mixture giving point 2 it is 0.5, and for the mixture giving point 3 it is 1.0. Since the mixtures giving the conversions represented by points 1 and 3 contain the same ratio of limestone to concentrates, the difference between these points cannot be attributed to a difference in the limestone to concentrates ratio.

The recycle to concentrates ratio for the mixture giving point 1 is 0; for the mixture giving point 2 it is 0.5, and for the mixture giving point 3 it is 1.0. Hence, it appears that for a given ratio of sodium carbonate to chromic oxide an increase in the recycle to concentrates ratio will lower the conversion. This indicates that the chromic oxide present in the recycle does not react as readily as does the chromic oxide present in the fresh concentrates.

From Figures 5 and 6 it appears that the three curves tend to converge at high ratios of sodium carbonate to chromic oxide. That is, the effect of increasing the ratio of recycle to concentrates becomes less

significant at higher ratios of sodium carbonate to chromic oxide. The effect of the recycle to concentrates ratio upon conversion should also be less when a recycle containing small amount of Cr_2O_3 is used.

In a previous study of this subject, Gore (2) investigated the effect of retention time, weight per cent sodium carbonate, diluent to concentrates ratio, and temperature upon conversion. For that study the mixtures did not contain a calcium compound. The highest per cent conversion obtained by Gore was 42.2 per cent, while the highest per cent conversion obtained in this study was 93.3 per cent. Since the conversions obtained for mixtures containing limestone are so much greater than for mixtures that do not contain limestone, it was attempted to relate the data obtained here to that obtained by Gore. For this purpose, two runs in addition to the runs listed on Table I were completed. The results of these two runs are tabulated in Table III on page 31. These two runs are plotted on Figure 7, page 40, together with two of the original points from this experiment and one point from Gore's work.

All points on Figure 7 have 22 weight per cent sodium carbonate and a diluent to concentrates ratio of 2. This, then, fixes a constant per cent concentrates of 26 and a constant per cent diluent of 52.

The composition of the diluent for points in Figure 7 varies from 100 per cent recycle to 100 per cent limestone. Hence, the ratio of limestone to concentrates varies from 0 to 2 and the ratio of recycle to

concentrates varies from 2 to 0. The recycle contains unreacted chrome and since the amount of recycle is changed from point to point, the ratio of sodium carbonate to chromic oxide also varies in Figure 7. In Figure 7 the per cent conversion is plotted vs. pounds of sodium carbonate to chromic oxide.

It may be observed from Figure 7 that as the ratio of sodium carbonate to chromic oxide is decreased, the per cent conversion decreases. It was shown above that an increase in the recycle to concentrates decreased conversion. Hence, the decrease in conversion shown in Figure 7 is in part due to an increase in the ratio of recycle to concentrates. It is also due in part to the decrease in the ratio of sodium carbonate to chromic oxide.

As the limestone to concentrates ratio decreases below 0.5 the decrease in per cent conversion is very sharp. This sharp decrease in per cent conversion is greater than would be expected as a result of the small changes in the sodium carbonate to chromic oxide ratio and in the recycle to concentrates ratio. Hence, it seems likely that for ratios of limestone to concentrates of 0.5 and below, a change in the proportion of limestone has an effect above that of a diluent.

On page 9 an analysis of a typical sample of chrome ore concentrates obtained from the Stillwater complex is given. It may be noted that these concentrates contain a considerable amount of silicon dioxide (6.88%). Hence, a possible explanation for the effect of low propor-

tions of limestone is that the calcium combines with silicon to form calcium silicate and thus prevents the combination of sodium, chromium, and silicon in an insoluble complex.

In order to present the data of Table I in a form having more meaning from a commercial standpoint, the data were converted to pounds of Cr_2O_3 converted per 100 pounds of charge. The data in this form are plotted in Figures 8, 9, and 10 on pages 41, 42, 43. In the above discussion it was noted that the higher diluent to concentrates ratio gave the higher per cent conversions. One may note from Figures 8, 9, and 10, that while the high diluent to concentrates ratio gave the higher per cent conversions, the lower ratio yields a greater amount of Cr_2O_3 converted per 100 pounds of charge.

Recommendations for Future Study

The results of this study indicate that for low ratios of limestone to concentrates a change in the proportion of limestone markedly affects the per cent conversion.

It was also shown in this study that an increase in the recycle to concentrates ratio for a given sodium carbonate to chromic oxide ratio decreases the per cent conversion and that this decrease becomes less significant as the ratio of sodium carbonate to chromic oxide increases.

An increase in the ratio of sodium carbonate to chromic oxide also increases conversion.

On the basis of these conclusions it is suggested that future study be given to mixtures containing a minimum amount of limestone to yield an effect other than that of a diluent, a large amount of concentrates, and a high ratio of sodium carbonate to chromic oxide. It must be noted, however, that these mixtures may not exceed 24 weight per cent sodium carbonate if they are to be utilized as a charge for a rotary kiln because of the balling effect. Mixtures for future study should also contain a minimum amount of recycle material and recycle materials containing small amounts of chromic oxide should be investigated.

CONCLUSIONS .

The per cent conversion obtained for this study was increased by increasing the temperature, by increasing the diluent to concentrates ratio and by increasing the amount of sodium carbonate. Introducing recycle as part of the diluent decreased the per cent conversion. This decrease became smaller as the amount of sodium carbonate in the mixture was increased and as the temperature was increased.

For a given ratio of sodium carbonate to chromic oxide, mixtures containing a greater proportion of recycle yield lower conversions.

At high ratios of limestone to concentrates a change in the proportion of limestone affected the conversion only by changing the sodium carbonate to chromic oxide ratio. At lower ratios, however, the limestone exhibited a greater effect.

The per cent conversions obtained for this study using limestone were much greater than were obtained in a previous study in which no calcium compound was used. This increase is due in part to the increase in sodium carbonate to chromic oxide ratio and in part to the decrease in recycle to concentrates ratio which results from replacing recycle by limestone. It is also partly due to the increase in the ratio of limestone to concentrates.

The amount of Cr_2O_3 converted per 100 pounds of charge was increased with an increase in temperature. However, a decrease in the diluent to

concentrates ratio increased the amount of Cr_2O_3 converted per 100 pounds of charge.

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TABLE II

ANALYSIS OF VARIANCE TABLE

Source	Degrees of Freedom	Sum of Squares	Mean Square	Mean Square Ratio	Significant F	
					5%	1%
A	2	429.6	214.8	45.7 ^{xx}	3.80	6.70
B	1	165.9	165.9	35.3 ^{xx}	4.67	9.07
C	1	490.5	490.5	100.1 ^{xx}	4.67	9.07
D	1	1,070.6	1,070.6	227.8 ^{xx}	4.67	9.07
AD	2	132.5	66.2	14.1 ^x	3.80	6.70
BC	1	12.8	12.8	2.7	4.67	9.07
BD	1	52.0	52.0	11.1 ^x	4.67	9.07
CD	1	17.3	17.3	3.7	4.67	9.07
Error	13	60.9	4.7			
Total	23	2,432.10				

x Significant on 99% level
 xx Highly significant (greater than 99%)

TABLE III

SPECIAL RUN

	No. 1	No. 2
Wt. % Na_2CO_3	22	22
<u># Diluent</u> # Concentrates	2	2
<u># Limestone</u> # Concentrates	0.25	0.12
Temperature	1900°F	1900°F
Conversion	54.0%	43.1%

TABLE IV
MEANS FOR FACTOR A

A ₁	A ₂	A ₃	Estimated Variance
74.0	79.6	84.3	0.77

TABLE V
MEANS FOR FACTOR B

B ₁	B ₂	Estimated Variance
76.7	81.9	0.62

TABLE VI
MEANS FOR FACTOR C

C ₁	C ₂	Estimated Variance
74.8	83.8	0.62

TABLE VII
MEANS FOR FACTOR D

	D ₁	D ₂	Estimated Variance
	86.0	72.6	0.62

TABLE VIII
TWO-WAY TABLE OF MEANS FOR FACTORS A AND D

	A ₁	A ₂	A ₃	Estimated Variance
D ₁	83.8	85.8	88.4	1.1
D ₂	64.2	73.5	80.2	

TABLE IX
TWO-WAY TABLE OF MEANS FOR FACTORS B AND D

	B ₁	B ₂	Estimated Variance
D ₁	84.8	87.1	0.88
D ₂	68.5	76.7	

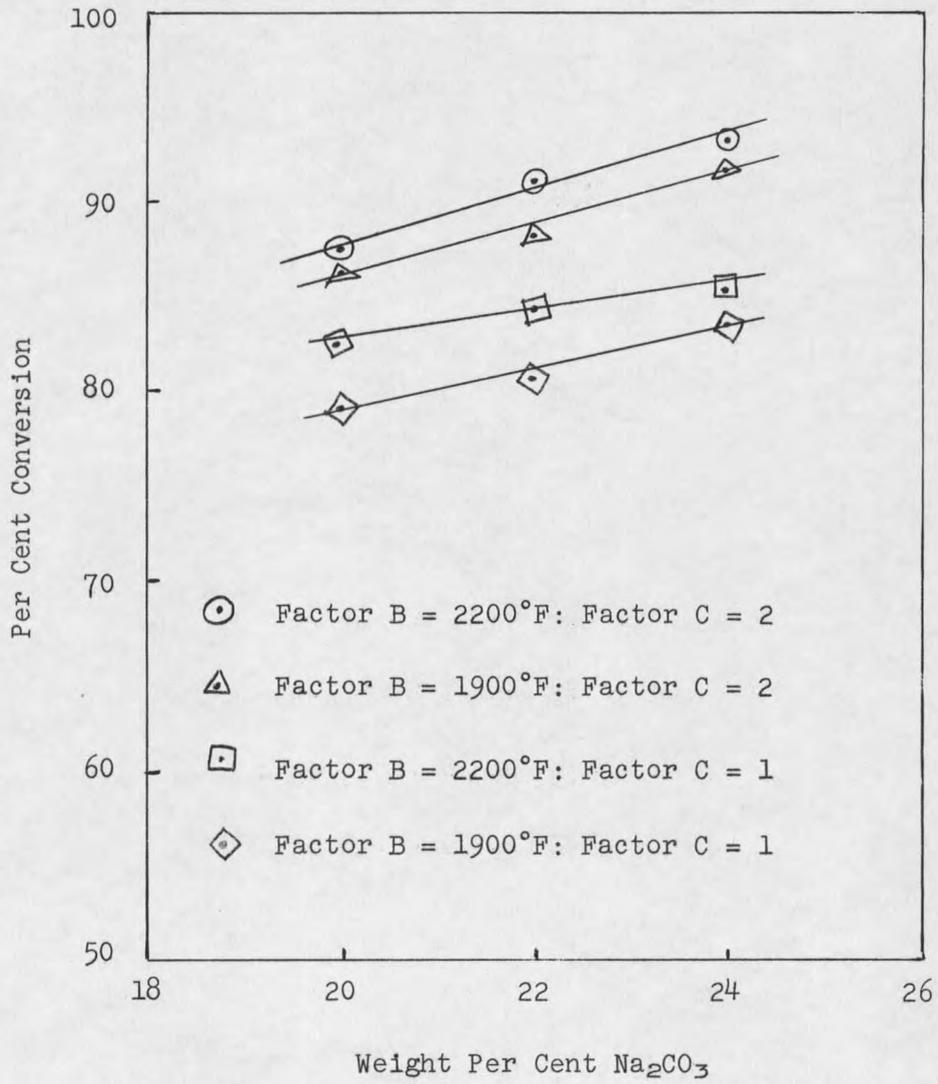


Figure 1. Plot of Per Cent Conversion vs. Per Cent Conversion for Mixtures Not Containing Recycle.

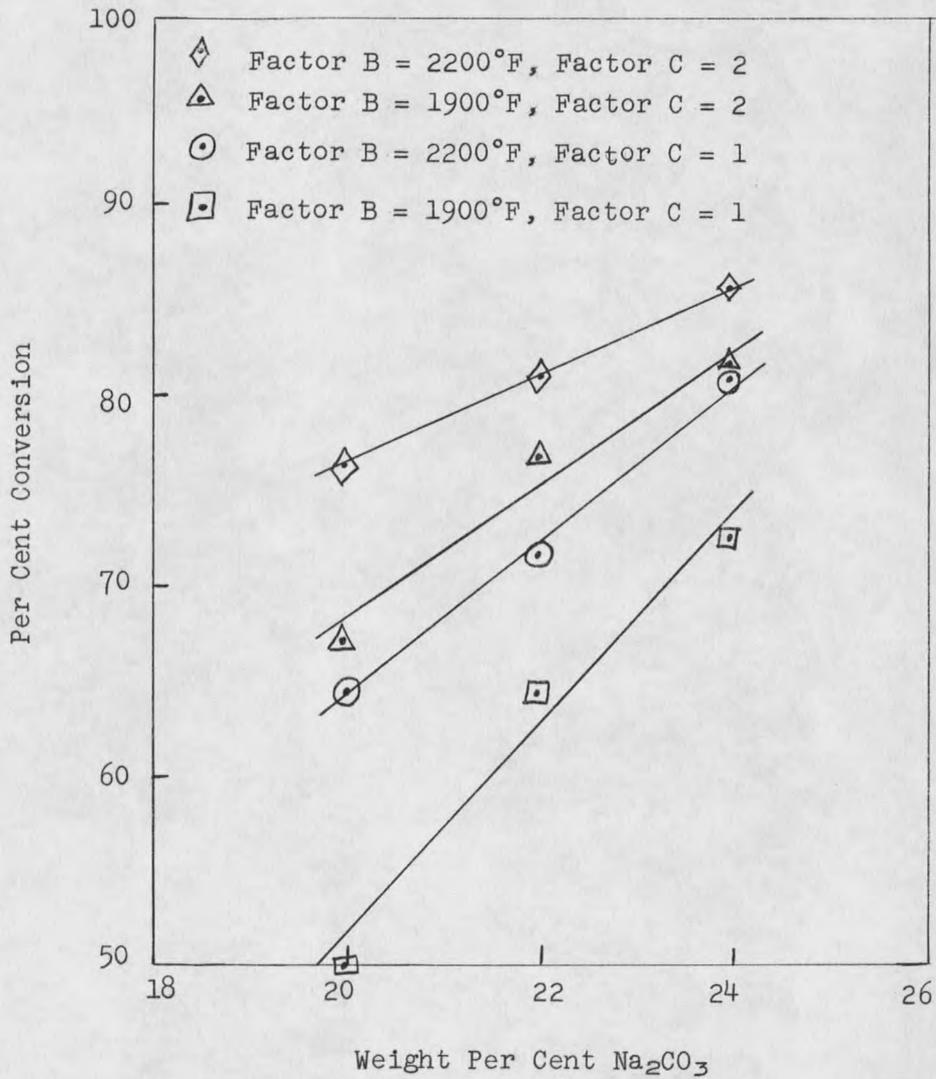


Figure 2. Plot of Per Cent Conversion vs. Weight Per Cent Na_2CO_3 for Mixtures Containing Recycle.

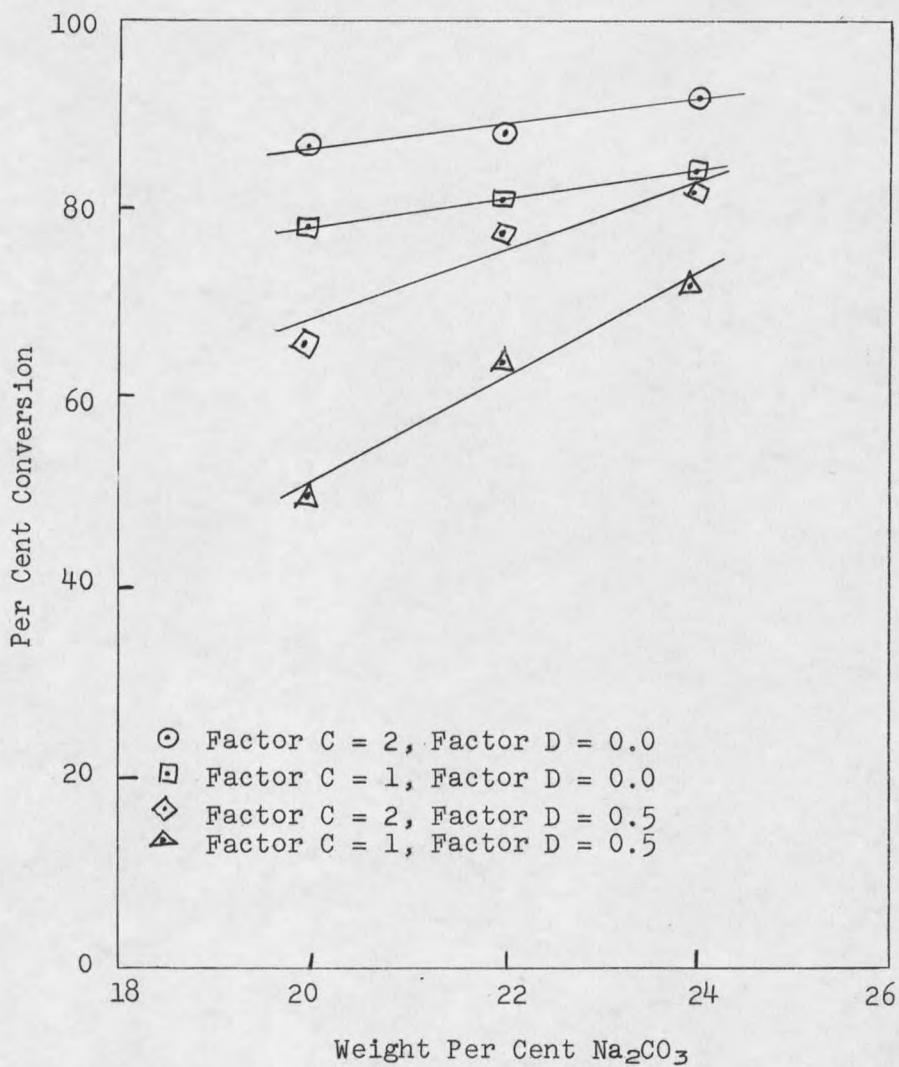


Figure 3. Plot of Per Cent Conversion vs. Weight Per Cent Na_2CO_3 for Samples Roasted at 1900°F.

