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# Chromium Recovery From High-Temperature Shift Cr-Fe Catalysts

By A. M. Stubbs and B. W. Jong

BUREAU OF MINES



UNITED STATES DEPARTMENT OF THE INTERIOR

**Report of Investigations 9204**

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**With an Appendix on Process Economics by M. J. Magyar**

**UNITED STATES DEPARTMENT OF THE INTERIOR  
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### UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	lb/d	pound per day
cm <sup>3</sup>	cubic centimeter	M gal	thousand gallon
ft	foot	min	minute
g	gram	mL	milliliter
gal	gallon	MMBtu	million British thermal units
g/L	gram per liter	mt	metric ton
h	hour	pct	percent
kW	kilowatt	ppm	part per million
L	liter	st	short ton
lb	pound	yr	year

# CHROMIUM RECOVERY FROM HIGH-TEMPERATURE SHIFT Cr-Fe WASTE CATALYST

By A. M. Stubbs<sup>1</sup> and B. W. Jong<sup>1</sup>

With an Appendix on Process Economics by M. J. Magyar

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## ABSTRACT

The Bureau of Mines has devised a procedure to selectively extract and recover chromic oxide ( $\text{Cr}_2\text{O}_3$ ) from waste high-temperature shift catalysts that contain approximately 6 pct Cr and 62 pct Fe, both in oxide form. The Bureau's procedure consists of roasting the waste catalyst with sodium hydroxide ( $\text{NaOH}$ ) or sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) followed by water leaching. The chromium from the leach liquor was recovered utilizing an oxidation-reduction reaction with pH adjustment to form a hydrous chromic oxide ( $\text{Cr}_2\text{O}_3 \cdot \text{XH}_2\text{O}$ ) precipitate. The roast-leach procedure produced chromium extractions greater than 89.7 pct, with product recovery in excess of 99 pct from the leach liquor.

The costs of the  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$  roast processes, including sizing and equipment-related recommendations, were determined by the Bureau's Office of Process Evaluation. The economic evaluation indicates that producing a  $\text{Cr}_2\text{O}_3$  product, at the present time, is not competitive with the present-day cost of imported chromites. The estimated average operating cost for both processes was \$5.44/lb of recovered  $\text{Cr}_2\text{O}_3$  concentrate. However, this procedure offers a potential alternative to the disposal of this waste through landfill.

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## INTRODUCTION

The United States is heavily dependent upon foreign sources for chromium to support its metallurgical, chemical, and refractory industries (1).<sup>2</sup> Therefore the Bureau of Mines has investigated several approaches for the recovery of chromium from waste catalysts.

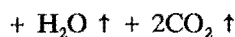
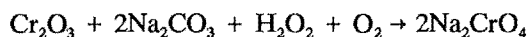
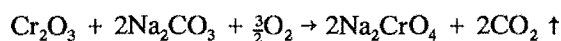
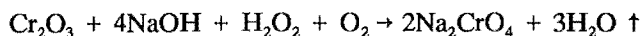
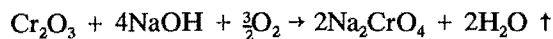
In the production of ammonia, a Cr-Fe containing catalyst is used at high temperatures to increase the hydrogen content of synthesis gas. After a period of time in use, this catalyst becomes contaminated with sulfur. At a predetermined point, the catalyst is discharged from the equipment and is considered a waste product. The waste product is generally disposed through landfill. To date, commercial recycling has not been justified because of transportation and refining costs, but most manufacturers express interest in obtaining an outlet for utilization of the waste catalyst rather than disposal in landfills (1).

There is 24.5 million lb of this type of catalyst in place (1). Annual catalyst discharge is 7 million lb, which amounts to an annual chromium loss of 420,000 lb. As of December 1985, the annual U.S. consumption of chromium was 585 million lb.

Previous Bureau work by Hundley (3), based partially on earlier work by Chandra (4), had demonstrated Cr could be recovered from various types of low-grade chromite ores using molten NaOH under oxidizing conditions. Current industry practices use Na<sub>2</sub>CO<sub>3</sub> and a lime (CaO) mixture to recover Cr from high-grade ores (4). At this time, few if any studies have been conducted aimed at recycling the metal content of high-temperature shift catalysts because of their low-chromium content and location (1).

The Bureau's approach to extract and recover Cr from spent high-temperature shift catalyst is shown in figure 1. Briefly, the procedure consisted of mixing the waste catalyst with a NaOH or Na<sub>2</sub>CO<sub>3</sub> reagent followed by addition of water. This mixture was then roasted at 600°

to 700° C to form sodium chromate (Na<sub>2</sub>CrO<sub>4</sub>). The catalyst was also mixed with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), reacted, and then mixed with a NaOH or Na<sub>2</sub>CO<sub>3</sub> solution and roasted at 600° to 700° C to form Na<sub>2</sub>CrO<sub>4</sub>. The basic reactions occurring during roasting of the waste catalyst using NaOH and Na<sub>2</sub>CO<sub>3</sub> with or without H<sub>2</sub>O<sub>2</sub> follow:



The roasted product was then ground and leached with hot water to extract the Cr. The leach liquor was treated by two different methods for Cr recovery. The first method used sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>) or sodium bisulfite (NaHSO<sub>3</sub>) for reduction of Cr to the trivalent form, followed by pH adjustment with sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) around 5.0 and NaOH pH adjustment to 7.5 for precipitation. The second method required that the pH be lowered with H<sub>2</sub>SO<sub>4</sub>, and then hydrazine (N<sub>2</sub>H<sub>4</sub>) was used as the reductant to adjust the pH. The precipitate produced by both methods, identified by X-ray diffraction, was of the form Cr<sub>2</sub>O<sub>3</sub>·xH<sub>2</sub>O, which agreed with the findings by Udy (5). The product was calcined at 350° C to produce Cr<sub>2</sub>O<sub>3</sub>. The waste solution produced from the precipitation was purified by stripping the Na<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> ions with an electro dialysis ion-selective membrane.

This report discusses the experimental results from laboratory-scale extraction and recovery studies of Cr from a Cr-Fe high-temperature shift catalyst. Reported are the optimized parameters for the unit operations of roasting, leaching, and product recovery.

<sup>2</sup>Italic numbers in parentheses refer to items in the list of references preceding the appendix at the end of this report.

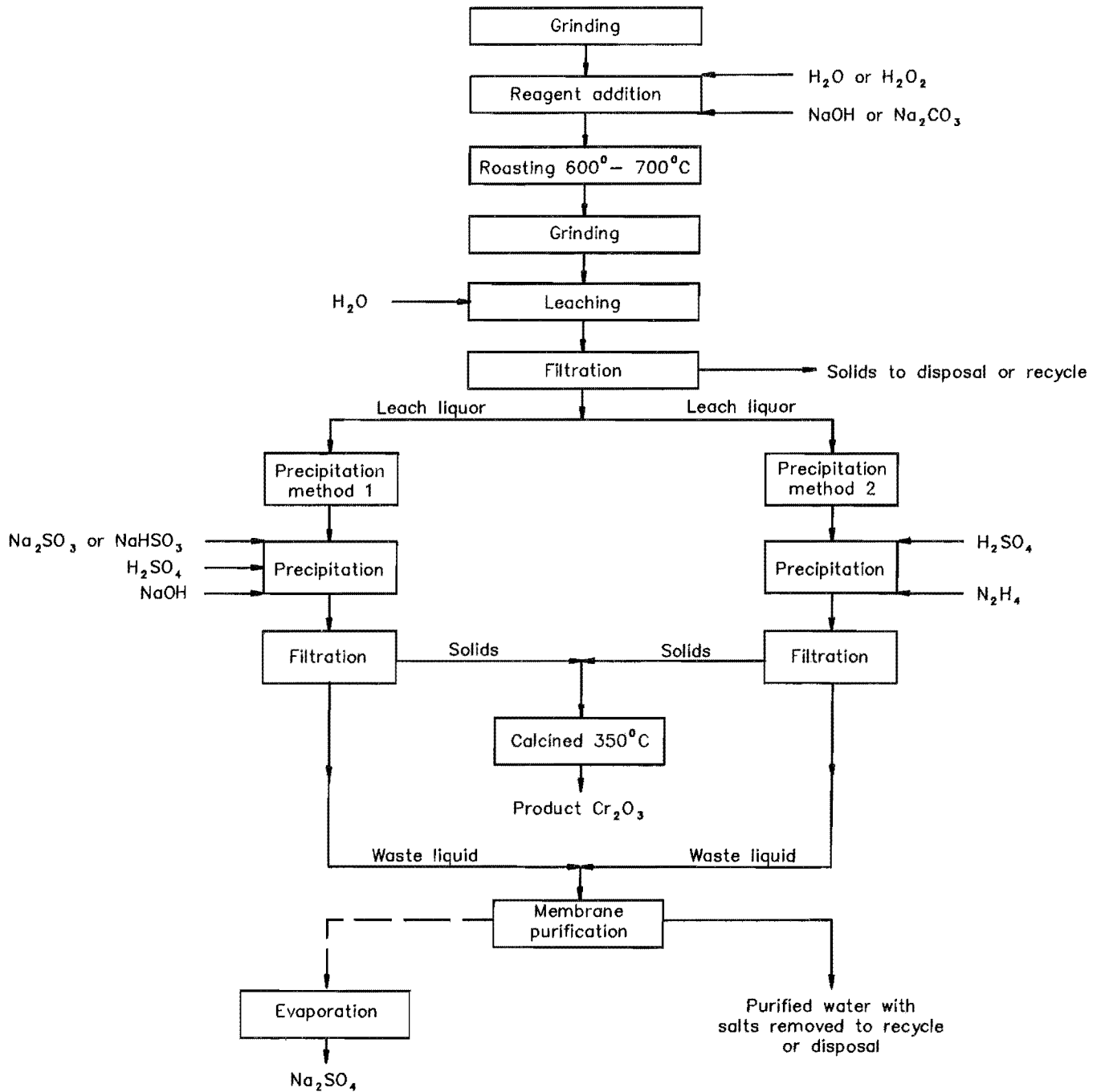


Figure 1.—Process flowsheet for Cr recovery from Cr-Fe waste high-temperature shift catalyst.



## RAW MATERIAL

The catalyst studied in this report was obtained from Inco Research & Development Center, Inc., Sterling Forest, Suffen NY through Bureau contract J0215042 (I). No information was obtained or given by Inco disclosing catalyst origin or if the sample was typical.

The catalyst was received in pellet form. The major phases in the pellets contained both  $\text{Cr}_2\text{O}_3$  and ferric oxide ( $\text{Fe}_2\text{O}_3$ ). Chemical analysis of the material showed that the catalyst contained 5.38 pct Cr, 61.3 pct Fe, 0.71 pct Ti, 0.61 pct Mg, 0.30 pct Mn, and 0.23 pct Si.

## EQUIPMENT AND EXPERIMENTAL PROCEDURES

The roasting of the waste catalyst was carried out in a small, 2,500-cm<sup>3</sup> muffle furnace with a 94-cm<sup>3</sup> high-temperature aluminum oxide ( $\text{Al}_2\text{O}_3$ ), ceramic crucible. No special mixing or gas injection system was used to enhance the roast or the subsequent water leach. Water leaching of the roasted product was done in a 250-mL, closed, three neck flask with agitation, followed by gravity filtration. Product precipitation was done in an open beaker with heating. Following the precipitation of the  $\text{Cr}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  product, salts in the residual solution were concentrated with an IONICS<sup>3</sup> MEDIMAT5 electro dialysis system with a Cr51CZ1386 cation, AR103QZL386 anion membrane to produce water for reuse or discharge.

Chromium extraction tests consisted of placing 6.0 g NaOH or 6.3 g  $\text{Na}_2\text{CO}_3$  in a high-temperature ceramic crucible with 25.0 g of catalyst, ground to minus 60-mesh. Twenty-three milliliters of water was added and the combination was mixed until the chemical reagent was dissolved. The reaction mixture was then roasted at 600° to 700° C for 2 h.

An alternate experimental method used 23 mL of 8.0 pct  $\text{H}_2\text{O}_2$  added to 25.0 g of minus 60-mesh catalyst. The mixture was allowed to react 8 to 10 min and NaOH or  $\text{Na}_2\text{CO}_3$  was then added, 6.0 and 6.3 g respectively, and allowed to dissolve. The mixture was roasted for 2 h at 600° to 700° C.

To determine the amount of Cr extracted from the waste catalyst, the roasted material, a lightly sintered, easily crushed mass, was ground to minus 60 mesh with mortar and pestle. The minus 60-mesh powder was water

leached at 5.0 pct solids for 2 h at 100° C and then gravity filtered. The leach liquor and solids were analyzed for Cr. The extraction percentage represented the amount of Cr in solution, based upon total Cr in the leach solution and remaining residue.

The method for recovering Cr from the leach liquor used either  $\text{Na}_2\text{SO}_3$  or  $\text{NaHSO}_3$  as reducing agents. The reducing agent was added as a powder in appropriate amounts based on 25 g/L of salt.  $\text{H}_2\text{SO}_4$  (12M) was added to reduce the 12.0 to 12.5 pH level to 3.1 to 5.0 with a pH of 5.0 being preferred to initiate the oxidation-reduction reaction between the  $\text{Na}_2\text{CrO}_4$ ,  $\text{NaHSO}_3$ , or  $\text{Na}_2\text{SO}_3$ , and the  $\text{H}_2\text{SO}_4$  in solution. Final pH adjustment to 6.8-7.5 was made by adding a 100-g/L-NaOH solution and heating to 60° to 65° C, which yielded the precipitated product.

A second Cr recovery method used the same pH adjustment. The pH level was then increased to 6.8-7.5 with a 35-pct solution of  $\text{N}_2\text{H}_4$ , which also served as the reductant, to form the precipitate. No external heat was necessary with this method.

The Cr recovery by both precipitation techniques was calculated as the amount precipitated from the leach liquor. The Cr precipitate produced by both recovery methods was calcined at 350° C for approximately 10 min to produce a dried  $\text{Cr}_2\text{O}_3$  product.

The variables studied in this investigation were the reagent-to-catalyst ratio, roast time, roast temperature, leach temperature, leach water volume, and the amounts of reductants used for chromium precipitation.

## RESULTS AND DISCUSSION

### CATALYST ROAST

The Cr-Fe waste catalyst (25.0 g) was initially roasted for 2 h using a 4:1 catalyst-to- $\text{Na}_2\text{CO}_3$  ratio. The roast was conducted using temperatures ranging from 500° to 900° C with the initial roast material in dry, paste, or wet form depending on test conditions. Results are shown in figure 2. Paste roasting with 15.0 mL of water produced the

highest extraction values at temperatures between 700° and 900° C. Extraction values of paste and dry roasting were similar at 600° C. Wet roasting with 30.0 mL of water showed poor extraction values at all temperatures, owing primarily to excessive spattering, and was not considered further. Dry roasting with no addition of water resulted in 5.0 to 6.0 pct lower extraction values than paste roasting at 700° C. Higher dry roasting temperatures to increase extractions were not attempted, since extrapolation of the dry roast data (fig. 2) indicated no significant advantage would likely result.

<sup>3</sup>References to specific products does not imply endorsement by the Bureau of Mines.

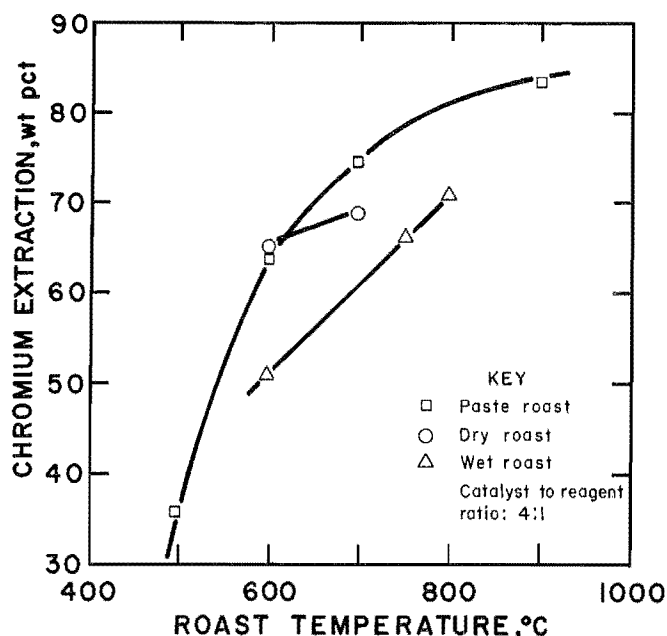


Figure 2.—Effect of roast temperature and material condition of Cr extraction.

An attempt was made at increasing the extraction efficiency by increasing the roast time of the dry roast from 2 h to 3 and 4 h at 600° and 700° C. The test results indicated (table 1) that extractions increased at 600° C giving comparable results to paste mixing at 700° C for 2 h (fig. 2), with an average extraction of 75.0 pct. The 700° C temperature produced extractions 3 to 4 pct lower than 600° C. This result is possibly due to carbonate loss at 700° C, which is 23.0 pct greater than at 600° C as shown in table 1. Dry roasting was discontinued, since paste roasting gave relatively the same extraction values with shorter roast times. Paste roasting at 700° C for 2 h was used as the standard roasting technique for further testing.

NaOH was substituted for Na<sub>2</sub>CO<sub>3</sub> at a weight ratio of 4.2:1 and paste roasted for 2 h at 700° C. The Cr extraction was 76.9 pct, which was comparable to the Na<sub>2</sub>CO<sub>3</sub> approach at 700° C as shown in figure 2.

The amount of water used to mix the catalyst and NaOH was increased from 15.0 to 23 mL, to increase reagent solubility; roast time and temperature remained constant. The metal extraction increased only from 76.9 to 78.9 pct.

Tests were run using catalyst-to-reagent weight ratios of 8.3:1, 4.2:1, 2.8:1, and 2.1:1 at 700° C for 2 h and using

TABLE 1. - Chromium extraction by dry roasting

Roast time, h	Roast temperature, °C	Extraction pct	Carbonate loss, pct
3	500	76.3	58.3
4	600	74.6	54.7
3	700	72.0	81.7
4	700	71.5	76.9

23 mL water with both NaOH and Na<sub>2</sub>CO<sub>3</sub>. The results are listed in table 2. Chromium extraction increased with decreasing ratio to 2.8:1 for NaOH (89.7 pct) and 2.1:1 for Na<sub>2</sub>CO<sub>3</sub> (90.9 pct). Results from NaOH tests showed an extraction decrease at a ratio of 2.1:1. Lowering the catalyst-to-NaOH ratio to 1.3:1 resulted in an extraction decrease to 47.0 pct.

H<sub>2</sub>O<sub>2</sub> was substituted for water in various concentrations ranging from 2.0 to 30.0 pct as an oxidizing agent, while maintaining previous experimental conditions at 700° C for 2 h and 23 mL of H<sub>2</sub>O<sub>2</sub> solution. Since an oxidizer was used, it was decided to maintain the amount of NaOH and Na<sub>2</sub>CO<sub>3</sub> used initially; i.e., 6.0 g NaOH and 6.3 g Na<sub>2</sub>CO<sub>3</sub>. The resulting Cr extraction utilizing NaOH and Na<sub>2</sub>CO<sub>3</sub> reagents ranged from 84.0 to 93.0 pct. NaOH produced 1.0 to 6.0 pct greater extractions than Na<sub>2</sub>CO<sub>3</sub> with the same H<sub>2</sub>O<sub>2</sub> addition (table 3).

Tests were run for both NaOH and Na<sub>2</sub>CO<sub>3</sub> at various catalyst-to-reagent ratios with 8.0 pct H<sub>2</sub>O<sub>2</sub> solution. The Cr extractions were higher than those obtained when water was used in the paste. The use of H<sub>2</sub>O<sub>2</sub> during the roast preparation increases extractions around 5.9 pct for NaOH solutions and 5.6 pct for Na<sub>2</sub>CO<sub>3</sub> solutions as shown in tables 2 and 4 and figure 3.

## LEACHING

Twenty-five grams of roasted product was initially leached in water at 5.0 pct solids, ambient pressure, and 100° C for 2 h to extract Cr as Na<sub>2</sub>CrO<sub>4</sub>. The Cr<sup>6+</sup> concentration produced under these conditions was 6.0 g/L with impurity levels of <0.1 ppm Mg and Mn, 7.5 ppm Ti, and 25 ppm Si. The impurity concentrations remained constant under extraction studies carried on

TABLE 2. - Chromium extraction for various water-mixed catalyst-to-roast reagent ratios, percent

Catalyst-to-reagent ratio	NaOH	Na <sub>2</sub> CO <sub>3</sub>
8.3:1	65.7	48.1
4.2:1	83.7	73.0
2.8:1	89.7	80.6
2.1:1	87.9	90.9

TABLE 3. - Chromium extraction using various amounts of H<sub>2</sub>O<sub>2</sub>, percent

(700° C for 2 with 4.2:1 catalyst-to-reagent ratio)

H <sub>2</sub> O <sub>2</sub> , pct	NaOH	Na <sub>2</sub> CO <sub>3</sub>
2.0	91.4	86.1
4.0	91.0	84.8
8.0	91.0	87.6
15.0	89.8	88.5
30.0	92.9	91.3

TABLE 4. - Chromium extraction for various H<sub>2</sub>O<sub>2</sub>-mixed catalyst-to-roast reagent ratios, percent

Catalyst-to-reagent ratio	NaOH	Na <sub>2</sub> CO <sub>3</sub>
8.3:1	72.2	49.7
4.2:1	91.0	87.6
2.8:1	96.2	84.0
2.1:1	85.9	93.7

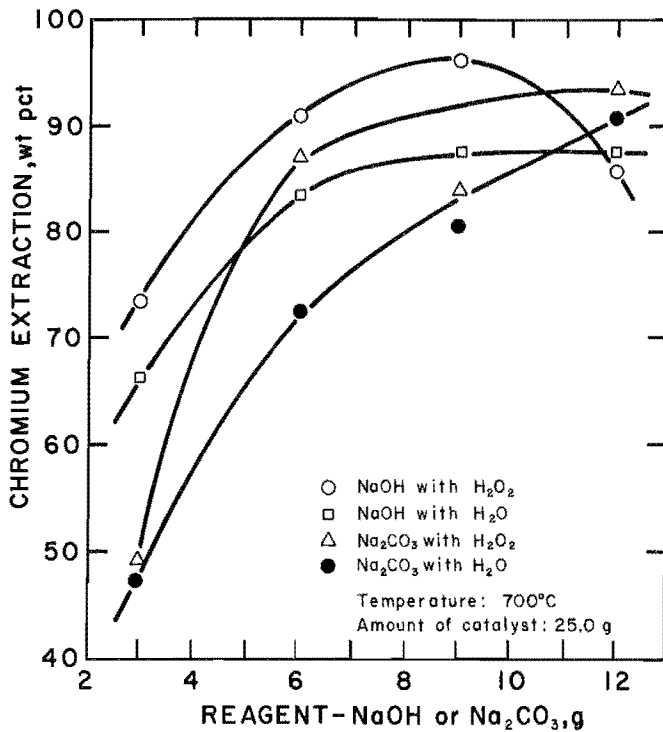


Figure 3.—Study of Cr extraction with varying reagent amount.

later. Extraction studies were made by varying the amount of water used, leach temperature, and leach time. Results are shown in table 5. Based on the extraction studies, the leaching conditions selected were 15.0 min of leach time, a leach slurry of 16 pct solids, and a temperature of 80° C to minimize evaporation from the solution while maintaining a high extraction. All tests were done with NaOH roasted product. These same preferred leaching conditions were applied to Na<sub>2</sub>CO<sub>3</sub> roast product (fig. 3).

### CHROMIUM PRECIPITATION

Cr<sub>2</sub>O<sub>3</sub> was chosen as the recovery product from the leach liquor. This decision was based partly on private communications with the officials in the waste catalyst regeneration industry. It was implied that the catalyst

TABLE 5. - Studies of atmospheric leach testing using NaOH solution

Varied leach slurry 100° C and 2 h		Varied leach temp at 16 pct solids and 2 h		Varied leach time at 16 pct solids and 100° C	
Solid, pct	Extraction, <sup>1</sup> pct	Temp, °C	Extraction, <sup>1</sup> pct	Time, h	Extraction, <sup>1</sup> pct
5.0	91.3	21.5	71.3	0.25	87.5
10.0	86.4	40.0	72.6	1.0	87.5
16.0	91.3	68.0	74.7	1.5	87.5
25.0	72.8	80.0	85.0	2.5	87.5
		100.0	91.3		

<sup>1</sup>Values were from stage leach testing and represent amount of Cr<sup>6+</sup> in solution.

manufacturers, which often retain rights over the waste catalysts, would likely require the metal recovered from catalysts to be returned. The decision to recover a Cr<sub>2</sub>O<sub>3</sub> product was also based on the relative simplicity of this approach.

The chromate ion was precipitated from the leach liquor through reduction to a chromic ion and then pH adjustment. Na<sub>2</sub>SO<sub>3</sub> or NaHSO<sub>3</sub> was added to the leach liquors in concentrations ranging from 10.0 to 60.0 g/L. The pH was lowered to 5.0 by addition of a concentrated H<sub>2</sub>SO<sub>4</sub> to allow reduction of Cr<sup>6+</sup> to Cr<sup>3+</sup>. The solution was then heated to 63° or 68° C. The pH was then readjusted with a NaOH solution to a level between 6.8 and 8.1. The Cr recovery from the leach liquors treated with Na<sub>2</sub>SO<sub>3</sub> was greater than 99.0 pct (table 6). Optimization of Cr recovery with NaHSO<sub>3</sub> was not done since the SO<sub>3</sub><sup>2-</sup> was oxidized in both Na<sub>2</sub>SO<sub>3</sub> and NaHSO<sub>3</sub> to SO<sub>4</sub><sup>2-</sup>. Product purity results indicate comparable products when either reducing agent was used (table 7). A pH adjustment to lower than 4.5 will produce unwanted hydroxides and/or sulfates.

Use of N<sub>2</sub>H<sub>4</sub> as a reducing agent for the chromate ion in leach liquors also was evaluated. A leach liquor volume of 0.15 L was mixed with various volumes of N<sub>2</sub>H<sub>4</sub>. Addition of N<sub>2</sub>H<sub>4</sub> to leach liquors increased the temperature from ambient to 35° to 40° C. N<sub>2</sub>H<sub>4</sub> was added at pH 5.0, which reduced the chromate ion from Cr<sup>6+</sup> to Cr<sup>3+</sup>, and resulted in a pH adjustment to a level between 6.8 and 7.4. The solutions were not heated as was the case with either Na<sub>2</sub>SO<sub>3</sub> or NaHSO<sub>3</sub>. Use of N<sub>2</sub>H<sub>4</sub> produces a comparable Cr recovery to the sulfites (99.0 pct or greater) as shown in table 6.

TABLE 6. - Studies of Cr recovery using Na<sub>2</sub>SO<sub>3</sub> and N<sub>2</sub>H<sub>4</sub>  
(0.15 L solution)

	NaOH		Na <sub>2</sub> CO <sub>3</sub>	
	Temp, °C	Recovery, pct	Temp, °C	Recovery, pct
Na <sub>2</sub> SO <sub>3</sub> , g/L:				
60	63	99.4	68	99.9
25	63	100	68	100
20	63	82.9	68	99.4
10	63	51.0	68	55.1
N <sub>2</sub> H <sub>4</sub> , mL:				
1.3	NAP	NAP	35	53.7
3.3	35	99.0	35	100
4.6	35	100	NAP	NAP
6.6	40	100	35	100
10	35	99.8	NAP	NAP

NAP Not applicable.

TABLE 7. - Purity of final Cr<sub>2</sub>O<sub>3</sub> products, percent

From NaOH solution using N <sub>2</sub> H <sub>4</sub>		From NaOH solution using NaHSO <sub>3</sub>		From Na <sub>2</sub> CO <sub>3</sub> solution using Na <sub>2</sub> SO <sub>3</sub>	
Compo- sition	Product	Compo- sition	Product	Compo- sition	Product
Cr <sub>2</sub> O <sub>3</sub>	94.66	Cr <sub>2</sub> O <sub>3</sub>	94.58	Cr <sub>2</sub> O <sub>3</sub>	92.45
Na <sup>+</sup>	3.09	Na <sup>+</sup>	1.39	Na <sup>+</sup>	5.45
SO <sub>4</sub> <sup>2+</sup>	2.25	SO <sub>4</sub> <sup>2+</sup>	4.03	SO <sub>4</sub> <sup>2+</sup>	1.94

The final product, identified as  $\text{Cr}_2\text{O}_3 \cdot \text{XH}_2\text{O}$ , was obtained by calcining the precipitated  $\text{Cr}_2\text{O}_3 \cdot \text{XH}_2\text{O}$  at  $350^\circ\text{C}$  for 5 to 10 min. The purity of the calcined  $\text{Cr}_2\text{O}_3$  product from NaOH leach solution using  $\text{N}_2\text{H}_4$  or  $\text{NaHSO}_3$  and the  $\text{Cr}_2\text{O}_3$  product from  $\text{Na}_2\text{CO}_3$  leach solution using  $\text{Na}_2\text{SO}_3$  is shown in table 7. Each method produced a product of 92 pct purity or greater.

### WASTE WATER TREATMENT

The waste water from the precipitation contained large quantities of  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  ions with less than 0.1 ppm  $\text{Cr}^{6+}$ . A membrane purification method, electro dialysis, stripped the ions and effectively purified the waste water. On the average, the procedure showed that about 70 pct of the waste water was suitable for recycling, the remaining 30 pct required further processing.

Ninety-eight pct of the  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  ions contains in the waste solution from the  $\text{Na}_2\text{CO}_3$  process were removed. Solutions from the NaOH process produced similar results of 99.2 pct removal. Waste treatment data are listed in table 8. Results show that the purified water

TABLE 8. - Results of waste water treatment, grams per liter

Salt	Feed	Water	
		Purified	Waste
NaOH WASTE SOLUTION			
$\text{Na}^+$ .....	4.80	0.02	16.60
$\text{SO}_4^{2-}$ .....	11.7	.05	8.38
$\text{Cr}^{6+}$ .....	$\leq .0001$	$\leq .0000312$	$\leq .0000688$
Na <sub>2</sub> CO <sub>3</sub> WASTE SOLUTION			
$\text{Na}^+$ .....	3.80	0.07	13.30
$\text{SO}_4^{2-}$ .....	8.44	.13	33.80
$\text{CO}_3^{2-}$ .....	.10	.06	.14
$\text{Cr}^{6+}$ .....	.0002	.0000591	.000141

containing less than 0.07 g/L  $\text{Na}^+$ , 0.13 g/L  $\text{SO}_4^{2-}$ , 0.06 g/L  $\text{CO}_3^{2-}$ , and 0.03 ppm  $\text{Cr}^{6+}$  can be recycled and used in the leaching circuit.

The waste water from the membrane system, which averaged 30 pct of the total sent to the electro dialysis unit, contained the concentrated  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  salts in solution. The solution at this point could possibly be evaporated to recover sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), but this was never actually attempted.

### PROCESS ECONOMICS

A preliminary economic evaluation on the proposed processes to extract and recover Cr from spent Cr-Fe waste high-temperature shift catalyst was prepared by the Bureau's Office of Process Evaluation.

The estimated capital costs of the plants, each designed to process 9,600 lb of the spent Cr-Fe catalysts, are \$3.9 million and \$4.2 million for the NaOH and the  $\text{Na}_2\text{CO}_3$  processes. Total operating costs were estimated to be \$5.41/lb and \$5.48/lb of recovered  $\text{Cr}_2\text{O}_3$  concentrate, for each process, respectively. The costs of the two processes are very close and can be considered to be same because of the estimating technique used for some of the equipment sizes and costs. High-cost items include raw materials at \$0.65/lb of product produced for the NaOH process and \$0.44/lb for the  $\text{Na}_2\text{CO}_3$  process. Both processes have high labor related charges of approximately \$2.00/lb of product, which include direct labor, plant maintenance, payroll overhead, and operating supplies.

Imported Turkish  $\text{Cr}_2\text{O}_3$  ore (48 pct  $\text{Cr}_2\text{O}_3$ ) costs \$125/mt f.o.b. and adjusting to 99 pct  $\text{Cr}_2\text{O}_3$ , yields a value

of \$258/mt or \$0.13/lb of  $\text{Cr}_2\text{O}_3$ . The currently designed catalyst plants, which are not optimum plant designs because of the limited amount of material, are uneconomical with operating costs of \$5.41/lb and \$5.48/lb of  $\text{Cr}_2\text{O}_3$  versus a  $\text{Cr}_2\text{O}_3$  value of \$0.13/lb.

However, the economic situation could improve if alternative  $\text{Cr}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  products are produced. An example of this would be to produce high-purity, pigment-grade  $\text{Cr}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ . Pure  $\text{Cr}_2\text{O}_3$  and pure  $\text{Fe}_2\text{O}_3$  sell at \$1.90/lb and \$0.30/lb, respectively, as pigments. Because of its larger quantity of iron (60 pct Fe versus 6 pct Cr in the waste Cr-Fe catalyst), the  $\text{Fe}_2\text{O}_3$  filter cake would have a value of \$2.93/lb of  $\text{Cr}_2\text{O}_3$  produced. Total value of the product would be \$4.83/lb of  $\text{Cr}_2\text{O}_3$  produced. The original object of this project was to recover Cr and not Fe. There is no information at this time on whether the necessary purity levels are attainable or what additional processing steps would be needed. Any further processing would increase both the capital and operating costs proportionately.

### CONCLUSIONS

Laboratory-scale testing was conducted by the Bureau to extract and recover Cr from waste Cr-Fe catalysts. The extraction procedure required that the catalyst be roasted with NaOH or  $\text{Na}_2\text{CO}_3$  followed by water leaching. The Cr extraction as  $\text{Na}_2\text{CrO}_4$  was greater than 89.7 pct. Recovery of as  $\text{Cr}_2\text{O}_3$  was through a reduction, a precipitation, and a calcination step that produced

recoveries of greater than 99 pct, generally leaving <0.02 ppm Cr in solution.

Cost studies were made on both NaOH and  $\text{Na}_2\text{CO}_3$  roast processes by the Bureau's Office of Process Evaluation. Based on the cost evaluation data, the plant would operate at 9,600 lb/d of waste catalyst processed for both processes. The total operating costs of the two

processes were found to be \$5.41/lb and \$5.48/lb of recovered  $\text{Cr}_2\text{O}_3$  product for each process respectively. The operating costs of the two processes are very close

with neither process offering a significant cost advantage. However, this procedure offers a potential alternative to the disposal of this waste through landfills.

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## APPENDIX.-PROCESS ECONOMICS

By M. J. Magyar<sup>1</sup>

Capital and operating costs for two plants are based on the process flowsheet presented in the main text. Each plant is designed to process 9,600 lb/d of spent Cr-Fe high-temperature shift catalysts to recover a Cr<sub>2</sub>O<sub>3</sub> product. Major items of equipment for both processes used for cost evaluation are shown in table A-1. The major difference between the two processes is material handling equipment necessary for the NaOH reagent (e.g., unloading, storage). Byproduct recovery was not included.

### CAPITAL COSTS

The capital costs estimate is of the general type called a study estimate by Weaver (6).<sup>2</sup> This type of cost estimate is usually expected to be within 30 pct of the cost for the plant described. However, recent studies on first-of-kind plants show that this kind of accuracy prediction is deceptive. Because of the limited engineering data available and the lack of impurity information, no accuracy limits for this evaluation are predicted.

The estimated fixed capital costs are \$3.6 million and \$3.9 million based on a first quarter 1987 basis (Marshall and Swift (M and S) index of 803.7) for plants processing 9,600 lb/d of spent Cr-Fe high-temperature shift catalysts. Capital costs are listed in Table A-2 for the two plants based on either a NaOH or a Na<sub>2</sub>CO<sub>3</sub> roast process. The plants operate 1 shift per day, 5 days per week, 330 days per year except for the roasting and product recovery sections, which operate 3 shifts per day 7 days per week. The remaining 35 days are for scheduled and unscheduled downtime.

Equipment costs used in this estimate are based on informal cost quotations from equipment manufacturers and on capacity cost data. In developing the plant capital costs, corrosion-resistant materials of construction are used where appropriate.

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<sup>2</sup>Italic numbers in parentheses refer to items in the list of references preceding the appendix.

TABLE A-1. - Major Items of equipment

Section and item	Quantity	Unit size
Reagent-feed preparation: Roll crusher	1	1 st/h
Roasting:		
Rotary kiln	1	2-ft diam by 21 ft
Rotary cooler	1	1.5-ft diam by 11 ft
Roll crusher	1	1 st/h
Leaching: Leach tank	1	2,900 gal
Precipitation: Precipitation tank	1	2,000 gal
Product recovery:		
Rotary dryer	1	2.7-ft diam by 44 ft
Membrane cell	1	400 cell pairs

Working capital is defined as the funds in addition to fixed capital, land investment, and startup costs that must be provided to operate the plant. Working capital, also shown in table A-2, is estimated from the following items: (1) raw materials and supplies inventory (costs of raw material and operating supplies for 30 days); (2) product and in-process inventory (total operating cost for 30 days); (3) accounts receivable (total operating cost for 30 days); (4) available cash (direct expenses for 30 days).

Startup costs are estimated as 10 pct of the fixed capital costs of which 1 pct is shown in table A-2. The remaining 9 pct is assumed to be first year operating costs; however, they are not shown in the operating cost table, but rather are used in calculating the required selling price. Land investment is not included in this estimate.

### OPERATING COSTS

The estimated annual operating costs for NaOH and Na<sub>2</sub>CO<sub>3</sub> processes are approximately \$1.3 million each as shown in Table A-3. An average of 330 days of operation per year is assumed over the life of the plants. Based on processing 9,600 lb/d of spent catalysts, this corresponds to an annual operating cost of \$0.41/lb of catalyst with an average cost of \$5.44/lb for each process. Operating costs are divided into direct, indirect, and fixed costs.

TABLE A-2.- Estimated capital costs:<sup>1</sup> NaOH roast process versus Na<sub>2</sub>CO<sub>3</sub> roast process

	NaOH roast	Na <sub>2</sub> CO <sub>3</sub> roast
Fixed capital:		
Reagent-feed preparation section . . . .	\$526,900	\$771,000
Roasting section . . . . .	729,200	722,000
Leaching section . . . . .	500,100	500,100
Precipitation section . . . . .	558,100	564,300
Product recovery section . . . . .	462,100	455,000
Steampant . . . . .	39,100	39,100
Subtotal . . . . .	2,815,500	3,051,500
Plant facilities, 10 pct of above		
subtotal . . . . .	281,600	305,200
Plant utilities, 12 pct of above		
subtotal . . . . .	337,900	366,200
Total plant cost . . . . .	3,435,000	3,722,900
Land cost . . . . .	0	0
Subtotal . . . . .	3,435,000	3,722,900
Interest during construction period . . .	143,100	155,200
Fixed capital cost . . . . .	3,578,100	3,878,100
Working capital:		
Raw material and supplies . . . . .	15,200	11,300
Product and in-process inventory . . . .	105,600	106,900
Accounts receivable . . . . .	105,600	106,900
Available cash . . . . .	59,500	57,500
Working capital cost . . . . .	285,900	282,600
Capitalized startup costs . . . . .	35,800	38,800
Total capital cost . . . . .	3,899,800	4,199,500

<sup>1</sup>Basis: M and S equipment cost index of 803.7.

Direct costs include raw materials, utilities, direct labor, plant maintenance, payroll overhead, and operating supplies. Raw materials and utility requirements per pound of  $\text{Cr}_2\text{O}_3$  are shown in table A-3. The direct labor cost is estimated on the basis of assigning 4.2 employees for each position that operates 24 h/d, 7 days per week and 1.0 employee for each position that operates 8 h/d, 5 days per week. Payroll overhead includes vacation, sick leave, social security, and fringe benefits.

Indirect costs include the expenses of control laboratories, accounting, plant protection and safety, plant administration, marketing, and company overhead. Research and overall company administrative costs outside the plant are not included.

Fixed costs include the cost of taxes (excluding income taxes), insurance, and depreciation. Depreciation is based on a straight-line, 10-yr period.

TABLE A-3. - Estimated annual operating costs: NaOH roast process versus  $\text{Na}_2\text{CO}_3$

	NaOH roast		$\text{Na}_2\text{CO}_3$ roast	
	Annual cost	Cost/lb $\text{Cr}_2\text{O}_3$	Annual cost	Cost/lb $\text{Cr}_2\text{O}_3$
Direct cost:				
Raw materials:				
Na <sub>2</sub> CO <sub>3</sub> at \$125.00 per ton . . . . .	NAP	NAP	\$78,700	\$0.331
NaOH at \$175.00 per ton . . . . .	\$144,400	\$0.608	14,400	.061
H <sub>2</sub> SO <sub>4</sub> at \$48.00 per ton . . . . .	8,700	.037	10,100	.043
Na <sub>2</sub> SO <sub>3</sub> at \$0.24 . . . . .	100	.001	100	.001
Chemicals for steamplant water treatment . . . . .	200	.001	200	.001
Total . . . . .	153,400	.647	103,500	.437
Utilities:				
Electric power at \$0.05/kW•h . . . . .	53,600	.226	60,100	.253
Process water at \$0.20/Mgal . . . . .	400	.002	400	.002
Natural gas at \$3.00/MMBtu . . . . .	58,100	.245	58,100	.245
Total . . . . .	112,100	.473	118,600	.500
Direct labor:				
Labor at \$10.50/h . . . . .	152,900	.644	152,900	.644
Supervision, 15 pct of labor . . . . .	22,900	.096	22,900	.096
Total . . . . .	175,800	.740	175,800	.740
Plant maintenance:				
Labor . . . . .	72,300	.304	78,400	.330
Supervision, 20 pct of maintenance labor . . . . .	14,500	.061	15,700	.066
Materials . . . . .	72,400	.305	78,300	.330
Total . . . . .	159,200	.670	172,400	.726
Payroll overhead, 35 pct of above payroll . . . . .	91,900	.387	94,500	.398
Operating supplies, 20 pct of plant maintenance . . . . .	31,800	.134	34,500	.145
Total direct cost . . . . .	724,200	3.051	699,300	2.946
Indirect cost, 40 pct of direct labor and maintenance . . . . .	134,000	.564	139,300	.586
Fixed cost:				
Taxes, 1.0 pct of total plant cost . . . . .	34,400	.145	37,200	.157
Insurance, 1.0 pct of total plant cost . . . . .	34,400	.145	37,200	.157
Depreciation, 10-yr life . . . . .	357,800	1.506	387,800	1.632
Total operating cost . . . . .	1,284,800	5.411	1,300,800	5.478

NAP Not applicable.