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# Study to Establish Cost Projections for Production of Redox Chemicals

J. F. Walther, C. C. Greco, R. N. Rusinko,  
and A. L. Wadsworth, 3rd  
Syracuse Research Laboratory  
Allied Chemical Company  
Allied Corporation

November 1982

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## SUMMARY

The objective of this study was to estimate manufacturing costs and selling prices of chromic chloride and ferrous chloride REDOX chemicals for the NASA REDOX ENERGY storage system. The results showed that the chemicals could be produced on a commodity scale for profitable sale at a cost-effective price for the REDOX system. Estimated prices for the chemicals from the two most favorable manufacturing processes corresponded to specific energy storage costs ranging from under \$9 to \$11/kWh.

The study was conducted in two parts: (1) a preliminary cost comparison of four different manufacturing processes and (2) a refined and expanded cost evaluation and cost sensitivity analysis of the most attractive process identified in the cost comparison. The cost estimates were based on grass-roots construction and operation of plants with capacities for 69000 metric tons per year of chromic chloride, anhydrous basis, and an equivalent amount of ferrous chloride, 54000 tons per year, anhydrous basis. The four proposed processes were:

- Reductive chlorination of chrome ore
- Chlorination of prereduced ore
- Electrolytic reduction of sodium chromate
- Methanol reduction of sodium chromate

The methanol process was selected as the most attractive for the refined and expanded analysis on the basis of cost, apparent technical feasibility, and commercial interest.

Projected price of REDOX chemicals for the base-case plant capacity of 69000 metric tons/year was \$1.26/kg of chromic chloride (anhydrous basis) including ferrous chloride. The selling price ranged from \$1.10/kg to \$1.68/kg when the plant capacity decreased from 138000 metric tons/year to 27680 tons per year. Cost sensitivity analysis showed that a 25% change in capital cost caused only a 8.7% change in price. Price was considerably less sensitive to changes in cost of individual raw materials and fuel.

The results support the NASA REDOX system as a potentially economically feasible device for bulk storage of electrical energy.

## INTRODUCTION

The NASA REDOX Energy Storage System is intended for bulk storage of electrical energy with potential applications for utility load-leveling and storage for solar photovoltaic and wind energy facilities. The advantages of the REDOX system over other advanced battery concepts derive from the simplicity of its design and electrochemical operation. It is a flowing electrolyte battery in which both electrode redox couples are fully dissolved in aqueous solutions at all states of charge. The solutions are stored outside the power cell stack in tanks and circulated through the cell during charging and discharging operations. The negative electrode couple, chromous/chromic ( $\text{Cr}^{+2}/\text{Cr}^{+3}$ ), and the positive electrode couple, ferric/ferrous ( $\text{Fe}^{+3}/\text{Fe}^{+2}$ ), are initially supplied to the system in the fully discharged state as chromic chloride and ferrous chloride in dilute hydrochloric acid solutions. These are the redox chemicals which are the subject of the present cost study.

The REDOX system, which has been under development at the NASA-Lewis Research Laboratories since 1974, is emerging as one of the more technically feasible devices for bulk storage of electrical energy among the various advanced batteries currently being developed. High round-trip energy efficiencies have been demonstrated, e.g., 75% at 300 amperes per square meter with a 310-square centimeter cell stack. No cycle life limitations have been observed during tens of thousands of deep-discharge cycles with a 310-square centimeter single cell (Ref. 1). The device construction and assembly is based on relatively inexpensive and existing electrodialysis and fuel cell technologies (Ref. 2), it operates at near ambient temperature and pressure, and it has minimal corrosion and sealing problems and minimal environmental and safety hazards. With its basic technical problems solved, it has strong potential for relatively near-term commercialization.

The economic feasibility of the device, however, has been under serious question because of concern over the cost and availability of the chromic chloride electrode reactant. A system cost study conducted by United Technologies Corporation showed that the price of chromic chloride could have a dominant impact on the total REDOX system cost (Ref. 2). This is shown in the following cost projection taken from the UTC study for production of one hundred 10 MW/100 MWh REDOX systems per year:

	Specific Energy Storage Cost, \$/kWh When $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ Price is	
	<u>\$2.86/kg</u>	<u>\$0.72/kg</u>
Chromic Chloride Storage Cost	56	14
Total System Cost	110	65

The system would be economically unattractive with chromic chloride at the 1980 market price (the time of the UTC study) of \$2.86/kg; but at one fourth this price, for example, the system cost would be competitive with other storage technologies and attractive for utility storage.

Early in the NASA REDOX program there was good reason to believe that the price of chromic chloride could be reduced substantially by use of a more direct production route from the ore and by achieving economy of large scale operation. Chromic chloride is a low volume chemical with little commercial value. It is produced in only ton quantities annually by several specialty chemical companies by chemical reduction of chromic acid (CrO<sub>3</sub>) in hydrochloric acid. Chromic acid, on the other hand, is produced in tens of thousands of tons annually; and even though it is made by a relatively lengthy step-wise conversion process from chromite ore, its price is a small fraction of the price of chromic chloride. The chromium value in the ore is first converted to sodium chromate which is then converted to sodium bichromate which is finally converted to chromic acid. The fact that unit costs can be reduced substantially through economy of scale is reflected in the following comparison of the annual U.S. production volumes and prices of these chrome chemicals. The price of chromic chloride, now offered at \$14.32/kg, is shown in the comparison to be 17-20 times higher than the prices of the commodity chromium chemicals from which it is produced when compared on the basis of contained chromium:

Chemical	U.S. Production Metric Tons/year	Present Price	
		\$/kg Chemical	\$/kg Contained Cr
Chromite Ore (45% Cr <sub>2</sub> O <sub>3</sub> )	183000(*)	0.08	0.12
Sodium Chromate, Anhyd.	-	1.39	4.32
Sodium Bichromate, Dihyd.	108000	1.26	3.60
Chromic Acid, CrO <sub>3</sub>	32000	2.27	4.36
Chromic Chloride, Hexahyd.	<10	14.32	73.35

\* Imported

The comparison suggests that the price of chromic chloride could be reduced to a level comparable to the prices of commodity chrome chemicals if it were produced on the same scale as the commodity chemicals and particularly if it were produced by a more direct route from the ore which by-passed production of sodium bichromate and chromic acid. Accordingly, the objective of this study was to estimate the costs for manufacture of chromic chloride and ferrous chloride REDOX chemicals on a scale corresponding to wide implementation of the NASA REDOX technology and using processes that are relatively direct routes from chrome ore. The study was conducted in two sequential tasks:



Task 1 -- A preliminary cost comparison of four proposed manufacturing processes. The comparison was based on grass-roots construction and operation of plants producing 69000 metric tons per year of chromic chloride, anhydrous basis, and an equivalent amount of ferrous chloride, 54000 metric tons per year, anhydrous basis.

Task 2 -- A refined manufacturing cost estimate of the most favorable process identified in Task 1. The refined cost estimate was then expanded from the base case plant capacity of 69000 metric tons to cost estimates for plant capacities of 27600 and 138000 metric tons per year, anhydrous basis. (These capacities correspond to 10000, 25000 and 50000 short tons per year of contained chromium.) Also, a cost sensitivity analysis was developed for the refined base case on variation in fixed capital, raw materials, and fuel oil. Finally, a relatively detailed flow sheet was prepared with mass balances, and a list was made of the major equipment items including specifications for sizes, ratings and materials of construction.

The four proposed processes chosen for the study were the following:

- Reductive chlorination of chrome ore
- Chlorination of prereduced chrome ore
- Electrolytic reduction of sodium chromate
- Methanol reduction of sodium chromate

Although only the first three processes were specified in the contract study, the methanol process was also evaluated because of favorable laboratory results obtained at the Syracuse Research Laboratory of Allied Chemical Corporation shortly before award of this contract.

The reductive chlorination process is the most direct route to chromic chloride from chromite ore. The process involves simultaneous reduction and chlorination of the ore at high temperature with coke and chlorine to produce vaporized chlorides of chromium, iron, aluminum and magnesium which are then isolated by selective condensation. The purified aluminum and magnesium chlorides can be sold for credit against the process costs. The basic concepts of this process were demonstrated on a laboratory scale by the U.S. Bureau of Mines in the 1930's (Ref. 3). Yields of chromic chloride and ferric chloride were greater than 90%. Pilot plant studies of essential components of the process were conducted successfully by Allied Chemical Company at the Syracuse Research Laboratory.

The chlorination of prereduced ore process is similar to the reductive chlorination process except that the coke reduction and chlorination operations are carried out separately. This process has a marked advantage over the single-step reductive chlorination process in that only chromium and iron chlorides are produced and very much smaller volumes of inert gasses are handled which, therefore, require smaller condensers. The process concept is based on results reported by the

U.S. Bureau of Mines which showed that up to 80% of the chromium and 90% of the iron in chromite ore can be reduced to their carbides by coke at 1300°C (Ref. 3). Furthermore, pilot plant studies at the Syracuse Research Laboratory of Allied Chemical Company showed that ferrochrome (iron and chromium carbides) can be readily converted into vaporized chromic chloride and ferric chloride by high temperature reaction with chlorine. The aluminum and magnesium values remain as inert oxides in this process.

The electrolytic and methanol reduction processes are similar to each other in that hexavalent sodium chromate or bichromate is reduced to the trivalent state by electricity in one case and by methanol in the other case. These processes also have in common the attractive feature that a major portion utilizes existing commercial technology for conversion of chromite ore to sodium chromate liquor. The concepts of these processes were based on results of laboratory studies at the Syracuse Research Laboratory of Allied Corporation on development of new routes to trivalent chromium compounds.

Although none of the processes have been demonstrated in full detail, they are amenable to relatively accurate cost evaluation according to procedures of sound engineering practice. Details of the processes are described in the next section.

## PROCESS DESCRIPTIONS

Four proposed processes were evaluated on the basis of grass-roots construction and operation of plants with capacities to produce 69000 metric tons per year chromic chloride and an equivalent amount of ferrous chloride, 54000 metric tons per year, both anhydrous basis. Descriptions of the processes follow.

### Reductive Chlorination of Chrome Ore

A flow diagram for the reductive chlorination process is shown in Figure 1. The final products are (1) anhydrous chromic chloride ( $\text{CrCl}_3$ ) blended with five mole percent chromous chloride ( $\text{CrCl}_2$ ) which is necessary to promote dissolution of the anhydrous product, (2) a saturated aqueous solution of ferrous chloride ( $\text{FeCl}_2$ ) (about 10 molar), (3) anhydrous aluminum chloride ( $\text{AlCl}_3$ ) and (4) hydrated magnesium chloride ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ). Credit for sale of the aluminum and magnesium chlorides was assumed in the analysis.

Only 67 percent of the required amount of  $\text{FeCl}_2$  is produced from the ore; the rest is made by a single-step reaction of scrap iron with hydrochloric acid (not shown in the flow chart). Overall yields of  $\text{CrCl}_3/\text{CrCl}_2$  from the ore is assumed to be 86 percent, and yield of  $\text{FeCl}_2$  from ore and scrap iron is assumed to be 99%.

Grade B chromite ore is introduced into a set of parallel reactors operated at  $950^\circ\text{C}$  where it is chlorinated using gaseous chlorine feed, coke as the reducing agent, and air.

Coke feed is based on optimizing the  $\text{CO}/\text{CO}_2$  mix in the off-gas to achieve the desired chlorination reactor temperature. The chlorination reaction is exothermic and is able to provide preheat for gas and solid feed streams and to maintain the reactors at the desired temperature.

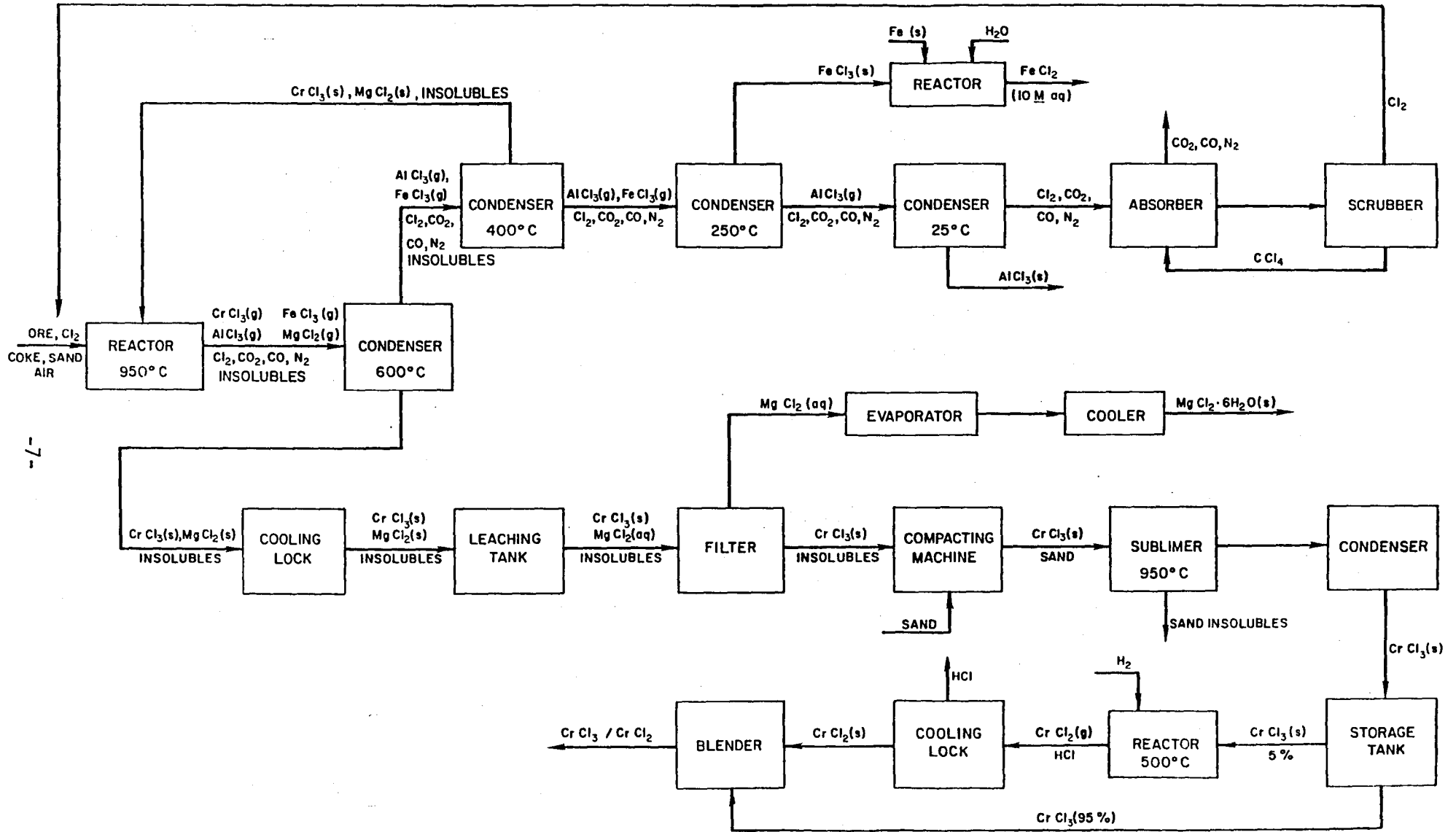
The chlorinator off-vapors (containing the metal chlorides and  $\text{Cl}_2$ ,  $\text{CO}/\text{CO}_2$ ,  $\text{N}_2$  and impurities) are cooled to  $600^\circ\text{C}$  in a set of parallel brick condensers where  $\text{CrCl}_3$  and  $\text{MgCl}_2$  are removed as solids.

The  $\text{CrCl}_3$  and  $\text{MgCl}_2$  solids are further cooled to room temperature and the mixture is leached with water. The leached product is filtered and the solution containing  $\text{MgCl}_2$  is evaporated whereby pure  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  is obtained.

The  $\text{CrCl}_3$  remaining in the filter cake is purified by means of a resublimation process at  $950^\circ\text{C}$  and a condensation step where pure  $\text{CrCl}_3$  is obtained. Because anhydrous  $\text{CrCl}_3$  is difficultly soluble in water, it is necessary to add to the  $\text{CrCl}_3$  small amounts of  $\text{CrCl}_2$ . The mixture  $\text{CrCl}_3/\text{CrCl}_2$  is readily soluble in water.

FIGURE 1

PROCESS SCHEME FOR REDUCTIVE CHLORINATION OF CHROME ORE



CrCl<sub>2</sub> is prepared by reducing CrCl<sub>3</sub> with hydrogen at 500°C. Five percent of the CrCl<sub>3</sub> obtained from the condenser is introduced into a hydrogenation reactor where it is converted to CrCl<sub>2</sub>. The hydrogen chloride by-product from the reduction reaction is cooled and scrubbed to produce concentrated acid.

The CrCl<sub>2</sub> is then blended with the CrCl<sub>3</sub> and the mixture sealed in air tight containers (to prevent aerial oxidation of CrCl<sub>2</sub>) for shipment to the site of the REDOX Storage System where it is dissolved in dilute hydrochloric acid.

The exhaust vapors of ferric chloride (FeCl<sub>3</sub>), AlCl<sub>3</sub>, Cl<sub>2</sub>, CO/CO<sub>2</sub> and N<sub>2</sub> from the CrCl<sub>3</sub>/MgCl<sub>2</sub> condensers are subjected to fractional condensation steps as follows:

A second condenser, which reduces the temperature of the gases from 600°C to 400°C, recovers the uncondensed CrCl<sub>3</sub>, MgCl<sub>2</sub> and insolubles. These products are recycled to the chlorination reactors. The off-gases from this second condenser are withdrawn to a FeCl<sub>3</sub> condenser where they are cooled from 400°C to 250°C at which temperature pure solid FeCl<sub>3</sub> is obtained.

The FeCl<sub>3</sub> is converted to FeCl<sub>2</sub> by reaction with metallic iron in an aqueous solution. Sufficient water is added to yield a saturated solution (about 10 molar) of FeCl<sub>2</sub>. The FeCl<sub>2</sub> is stored in sealed containers, protected from aerial oxidation, for shipment to the site of the REDOX Storage System.

The remaining vapor from the FeCl<sub>3</sub> condenser is introduced into an AlCl<sub>3</sub> condenser where pure AlCl<sub>3</sub> is obtained.

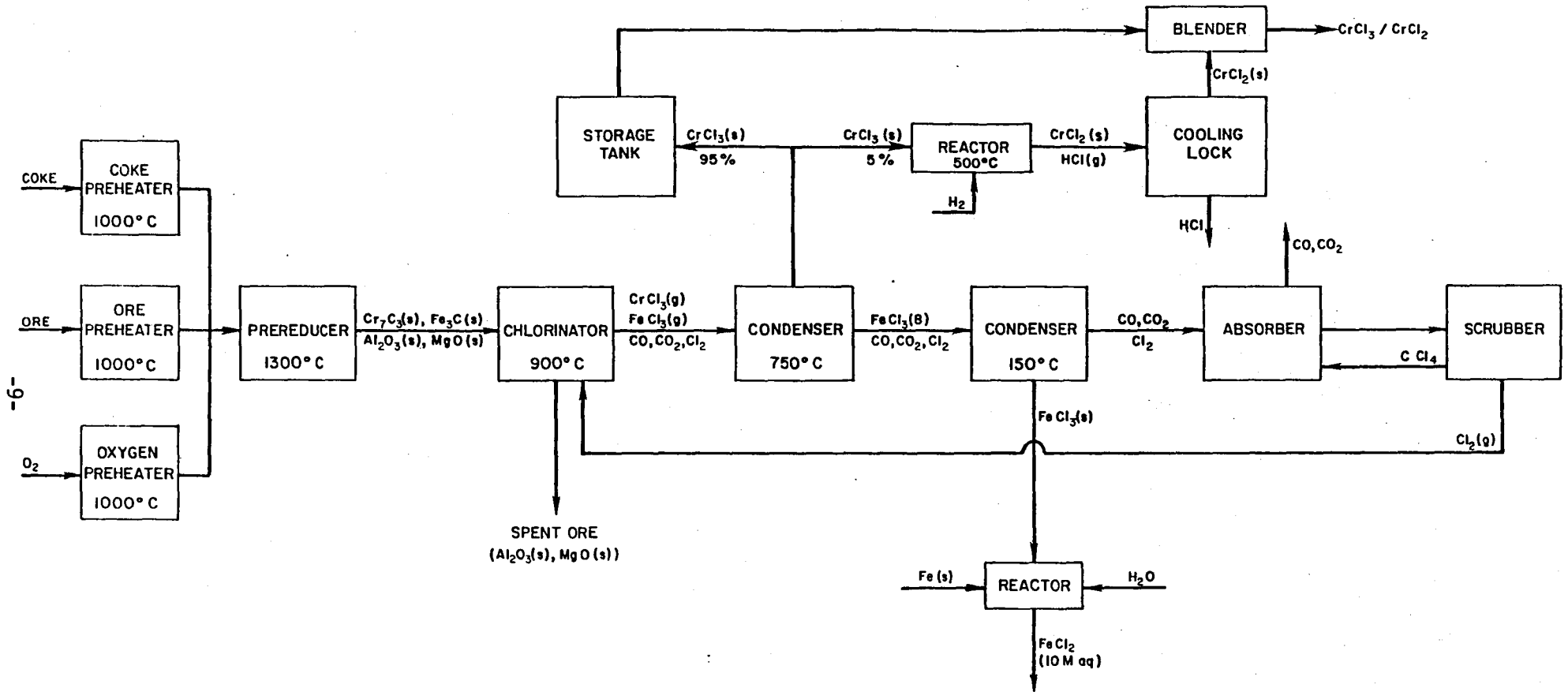
The exhausted gases from the AlCl<sub>3</sub> condenser are sent to a chlorine recovery system consisting of a carbon tetrachloride adsorption/stripper unit. The Cl<sub>2</sub> stripped from the system is returned to the main chlorination reactors.

#### Chlorination of Prerduced Chrome Ore

A flow diagram of the process for chlorination of prerduced chrome ore is shown in Figure 2. Final products of this process are (1) anhydrous chromic chloride blended with five mole percent chromous chloride to promote dissolution and (2) a saturated aqueous solution of ferrous chloride (about 10 molar). As in the reductive chlorination process, 33 percent of the ferrous chloride is made by reaction of hydrochloric acid with scrap iron (not shown); the rest of the ferrous chloride is derived from the chrome ore.

FIGURE 2

PROCESS SCHEME FOR CHLORINATION OF PREREDUCED CHROME ORE



Overall yield of  $\text{CrCl}_3/\text{CrCl}_2$  is assumed to be 86 percent and of  $\text{FeCl}_2$  from ore and scrap iron is assumed to be 99 percent.

Grade B chromite ore, coke, and oxygen are preheated before they are introduced into the reducing reactors since the prereduction reaction of chromite ore is strongly endothermic. The temperature in the reducing kiln is maintained at  $1300^\circ\text{C}$  to insure rapid conversion of the chromium and iron oxides to the corresponding carbides. Other products include the oxides of magnesium and aluminum as well as the off vapors,  $\text{CO}$  and  $\text{CO}_2$ .

Solids from the prereducing kiln are fed together with  $\text{Cl}_2$  into a chlorinator. The chlorination reaction is exothermic and maintains the reactor at  $900^\circ\text{C}$ . The magnesium and aluminum oxides remain inert throughout the chlorination process and are removed as spent ore. The chlorination off-vapors,  $\text{FeCl}_3$ ,  $\text{CrCl}_3$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{Cl}_2$ , are cooled to  $750^\circ\text{C}$  in a set of brick condensers where  $\text{CrCl}_3$  selectively condenses as a solid.

Small amounts of  $\text{CrCl}_2$  must be added to anhydrous  $\text{CrCl}_3$  in order to promote solubility in water. Chromous chloride is produced by reducing  $\text{CrCl}_3$  with hydrogen gas at  $500^\circ\text{C}$ . Five percent of the condensed  $\text{CrCl}_3$  is introduced into a hydrogenation reactor where it is reduced to  $\text{CrCl}_2$ . The products,  $\text{CrCl}_2$  and  $\text{HCl}$ , are passed to a cooling lock where  $\text{CrCl}_2$  is isolated as a solid. The  $\text{HCl}$  is cooled and scrubbed to produce concentrated acid.

The  $\text{CrCl}_2$  and  $\text{CrCl}_3$  are then combined and the mixture is sealed in air tight containers to prevent aerial oxidation of  $\text{CrCl}_2$ . This mixture can be dissolved in dilute hydrochloric acid after shipment to the site of the REDOX Storage System.

The exhaust vapors from the  $\text{CrCl}_3$  condenser,  $\text{FeCl}_3$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{Cl}_2$ , are passed into a condenser cooled to  $150^\circ\text{C}$  where  $\text{FeCl}_3$  solidifies. Off-gases from the  $\text{FeCl}_3$  condenser,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{Cl}_2$ , are passed to a chlorine recovery system. The  $\text{Cl}_2$  stripped from the system is returned to the chlorination reactors.

The ferrous chloride is converted from  $\text{FeCl}_3$  by reduction with metallic iron in aqueous solution. Sufficient water is added to produce a saturated solution (5 molar) of  $\text{FeCl}_2$ . The  $\text{FeCl}_2$  is shipped to the REDOX Storage System in sealed containers protected against air oxidation.

## Electrolytic Reduction of Sodium Chromate

The flow diagram for this process is shown in Figure 3. The front end of the process, sodium chromate production, utilizes present commercial manufacturing technology for chrome chemicals. Yield of chromium value is assumed to be 85 percent for sodium chromate production and with additional small losses in the rest of the process, 82 percent overall.

Grade B chrome ore is crushed, dried, and ground in ball mills to a fineness of 90-98 percent through 200 mesh. The pulverized ore is then mixed with soda ash and a diluent consisting of dried ground ore residue from previous operation.

After thorough blending, the mixture is roasted in oil-fired rotary kilns in which an oxidizing atmosphere is maintained. Temperature in the firing zone is closely controlled at 1100-1150°C. Time for passage of the material through the kiln is of the order of four hours.

The product from the kiln passes through a rotary cooler where it is cooled and the air used for combustion in the kiln is preheated. The cooled product then is leached to dissolve the sodium chromate in false-bottomed boxes called filters. Liquid is pumped onto the top of the charge, percolates downward, and is drawn off as a clear solution at the bottom. A battery of filters is arranged for countercurrent leaching, and a nearly saturated solution is obtained.

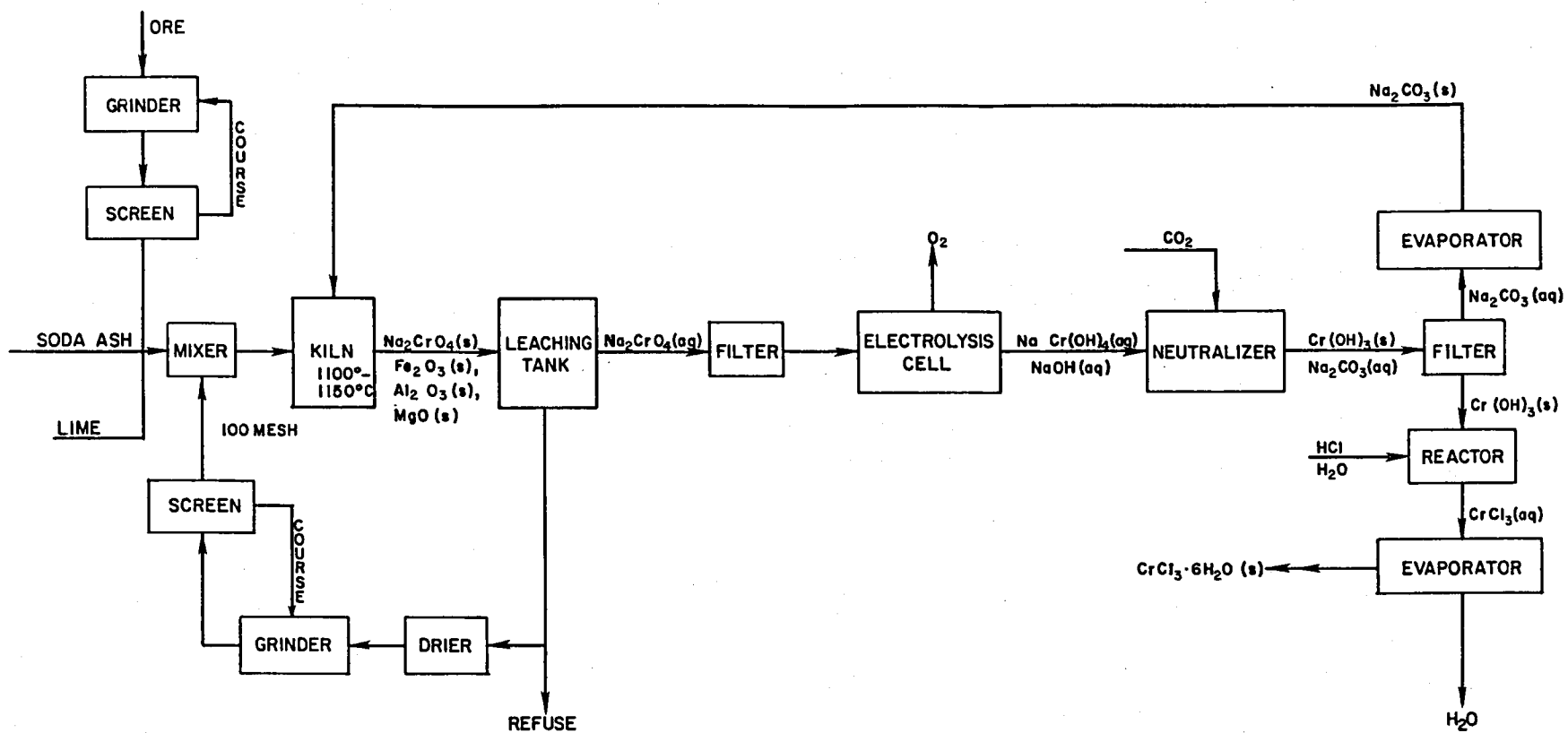
Part of the residue from leaching is dried, ground to pass 100 mesh, and is recycled as a diluent in the original mix, as described above. The remainder is discarded.

Sodium chromate in the yellow liquor is reduced to trivalent sodium chromite ( $\text{NaCr}(\text{OH})_4$ ), and sodium hydroxide ( $\text{NaOH}$ ) by cathodic reduction in electrolytic cells. The oxidation product,  $\text{O}_2$ , at the anode is discharged to the atmosphere. Current efficiency for the cathode reaction is assumed to be 60 percent at a cell voltage of 3.5 V and current density of 2000 A/m<sup>2</sup>.



FIGURE 3

PROCESS SCHEME FOR ELECTROLYTIC REDUCTION OF SODIUM CHROMATE



Isolation of trivalent chromium from the sodium ions is accomplished by neutralization and filtration operations. Carbon dioxide is added to the  $\text{NaCr(OH)}_4/\text{NaOH}$  catholyte to decrease the basicity of the solution and cause hydrous chromic hydroxide ( $\text{Cr(OH)}_3$ ) to precipitate. The soluble product, sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), contains all the sodium ions. Filtration separates solid  $\text{Cr(OH)}_3$  from the  $\text{Na}_2\text{CO}_3$  solutions.

Water is stripped from the  $\text{Na}_2\text{CO}_3$  solution and the solid soda ash is recycled to the ore roasting operation.

The solid  $\text{Cr(OH)}_3$  from the filtration step is converted to a 2 molar solution of  $\text{CrCl}_3$  by reaction with  $\text{HCl}$  and  $\text{H}_2\text{O}$  in a reactor. Evaporation of the solution yields the solid product  $\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$  which is packaged for shipping.

Ferrous chloride is produced separately as a saturated solution (about five molar) by a single-step reaction of scrap iron with hydrochloric acid (not shown).

#### Methanol Reduction of Sodium Chromate

The flow diagram for this process is shown in Figure 4. As with the electrolytic process, the section for production of sodium chromate yellow liquor utilizes present commercial manufacturing technology for chrome chemicals. Yield of chromium value is assumed to be 85 percent for sodium chromate production and 82% overall.

Production of sodium chromate yellow liquor was described previously for the electrolytic reduction process. In a single reduction operation, the yellow liquor is acidified with hydrochloric acid and the resultant sodium bichromate is reduced to  $\text{CrCl}_3$  with excess methanol. The  $\text{CO}_2$  by-product is discharged to the atmosphere. The reduced solution is cooled, the sodium chloride product crystallized out and separated by filtration.

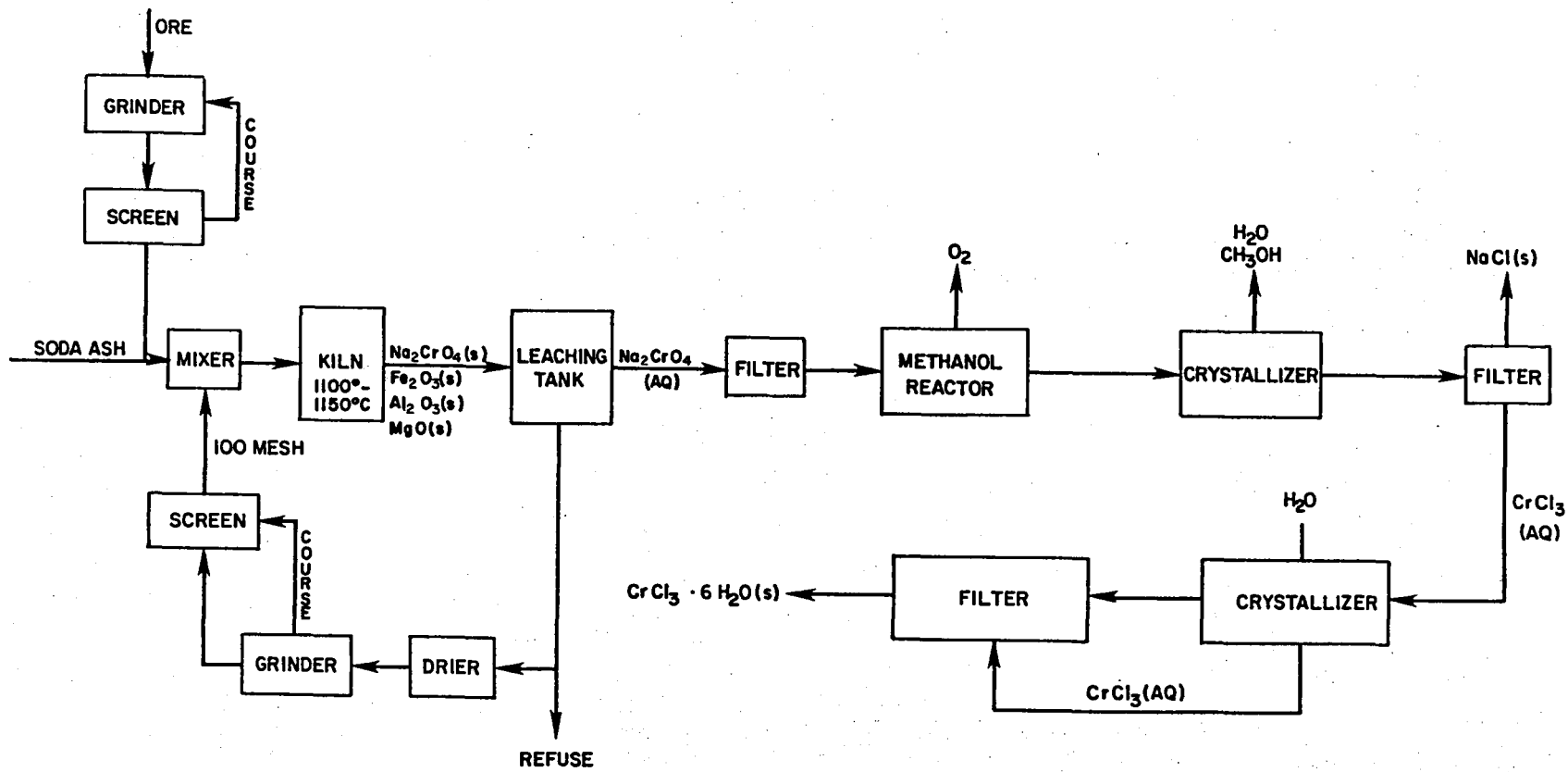
Chromic chloride hexahydrate is isolated by evaporation and crystallization.

Excess methanol is recovered from  $\text{CrCl}_3$  evaporator, purified by distillation, and recycled to the chromate reduction reaction.

Ferrous chloride is produced separately as a saturated solution (about 5 molar) by a single-step reaction of scrap iron with hydrochloric acid (not shown). Yield is assumed to be 99 percent.

FIGURE 4

PROCESS SCHEME FOR METHANOL REDUCTION OF SODIUM CHROMATE



RESULTS AND DISCUSSION OF TASK 1  
PRELIMINARY COST COMPARISON

Task 1 Cost Summary

Two of the processes were projected to yield selling prices of REDOX chemicals equal to or below the NASA objective of \$1.19/kg anhydrous chromic chloride. Chlorination of prereduced chrome ore and methanol reduction of sodium chromate were projected to be the lowest cost processes yielding estimated selling prices of, respectively, \$0.99 and \$1.23/kg anhydrous chromic chloride. It should be noted that these prices include an equivalent quantity of co-product ferrous chloride, whereas the NASA objective was for chromic chloride alone.

Estimated selling prices of REDOX chemicals from the four processes ranged from \$0.99 to \$1.91/kg anhydrous chromic chloride as shown in Table I.

TABLE I  
ESTIMATED SELLING PRICE OF  
CHROMIC CHLORIDE AND FERROUS CHLORIDE  
(LAST HALF 1981 DOLLARS)  
(30% ROI, FOB PLANT)

Manufacturing Process	\$/kg Anhydrous CrCl <sub>3</sub> , Including FeCl <sub>2</sub>
Chlorination of Prereduced Chrome Ore	0.99
Methanol Reduction of Sodium Chromate	1.23
Electrolytic Reduction of Sodium Chromate	1.49
Reductive Chlorination of Chrome Ore	1.91

Projected energy storage costs corresponding to the price estimates at 30% before-tax return on investment (ROI) for chromic chloride and ferrous chloride and purchased hydrochloric acid are compared in Table II. The projections were based on the same system operating parameters and assumptions utilized in recently published cost projections for REDOX Energy Storage Systems (Ref. 2), except that the storage costs presented here correspond to initial storage capacity. They do not include make-up chemicals that would be required because of losses over years of REDOX system operation (see Study Discussion section for details). Projected energy storage costs for chemicals from the two lowest cost processes ranged from \$8.48 to \$11.06/kWh for 500-kWh and 100-MWh REDOX batteries. These costs are considerably more attractive than the previous projections of \$25 and \$22/kWh, respectively, for the two battery sizes.

In light of the chemical price estimates for the two lowest cost processes in this study, total manufacturer's selling price for REDOX systems can be reduced from the earlier projections, which ranged from \$63 to \$116/kWh, depending on the assumed cost of the chemicals (Ref. 2), to \$54-59/kWh for the 500-kWh system and to \$51-53/kWh for the 100-MWh system.

TABLE II  
PROJECTED ENERGY STORAGE COSTS FOR  
REDOX CHEMICALS, INCLUDING PURCHASED  
HYDROCHLORIC ACID  
(1981 DOLLARS)

Manufacturing Process	Energy Storage Cost, \$/kWh	
	10 kW/500 kWh Battery	10 MW/100 MWh Battery
Chlorination of Prereduced Chrome Ore	8.97	8.48
Methanol Reduction of Sodium Chromate	11.06	10.50
Electrolytic Reduction of Sodium Chromate	13.42	12.77
Reductive Chlorination of Chrome Ore	17.09	16.30

A recommendation was made to NASA-Lewis REDOX program management, and accepted, that Task 2 should be undertaken to perform the refined cost study and sensitivity analysis on the methanol reduction process. This process is believed to be the best defined technically of all the processes and has the greatest probability for development to commercial success. It also may be the most desirable process from a commercial standpoint because it would allow coproduction of present commercially important chrome chemicals, and it could utilize an existing chromic acid plant where capacity is available.

### Discussion of Task 1 Results

Capital requirements for the four processes are itemized in Table III, including fixed capital, working capital, and cost of technology (R&D). Chlorination of prereduced ore and methanol reduction of sodium chromate are projected to have comparable investment requirements, \$72 million, which are considerably lower than the other two processes, \$110 million for electrolytic reduction and \$275 million for reductive chlorination. The large fixed capital requirement for the reductive chlorination process is associated with the extraordinarily large brick condensers which would occupy an area of about six acres. The condensers have to be this large in order to handle the voluminous quantities of combustion air gases and chlorine at low enough velocity so as to avoid entrainment of the metal halide condensates. In contrast, the process of chlorination of prereduced ores does not pass combustion air through the system and, consequently, the condensers would be only one twentieth as big. Besides the cost factor, the technical feasibility of condenser sections of the reductive chlorination process is questionable.

The higher capital cost for the electrolytic process is associated with the cost of the electrolysis cells. Electrolysis cells are shown to be expensive forms of reactors.

Annual operating costs and charges for the four processes are itemized in Tables IV and V. Reductive chlorination of chrome ore is projected to have one of the lowest net operating costs because of credits taken for sale of by-products. This is in spite of high estimated maintenance costs. The estimated selling price of REDOX chemicals from this process, however, is highest because of the very large capital requirements. The electrolytic reduction process has the highest operating costs, \$71 million, largely because of high electricity charges to operate the cells.

Energy storage costs for REDOX chemicals based on the estimated selling prices from the four processes were given earlier in Table II. The costs include purchased hydrochloric acid.

TABLE III  
CAPITAL INVESTMENT FOR MANUFACTURE OF REDOX CHEMICALS  
(69000 METRIC TONS/YEAR CrCl<sub>3</sub>, 54000 METRIC TONS/YEAR FeCl<sub>2</sub>)  
(k\$, 1981)

Manufacturing Process	Reductive Chlorination of Chrome Ore		Chlorination of Pre-Reduced Ore	Electrolytic Reduction of Sodium Chromate	Methanol Reduction of Sodium Chromate
	1 atm	3 atm		2000 A/m <sup>2</sup>	
<b>Operating Conditions</b>					
<b>Fixed Capital</b>					
<b>Major Equipment Installed</b>					
Raw Materials Handling	2,330	2,330	2,126	2,245	2,245
Roasting				3,035	3,035
Leaching and Yellow Liquor Purification				3,155	3,155
Prereducers			2,230		
Chlorinators			2,230		
Chloride Production	15,815	5,510			
Electrolysis				15,427	
1st Reactor Condensers	6,405	2,605			
2nd Reactor Condensers	4,500	1,500			
FeCl <sub>3</sub> Condensers	3,500	1,320	300		
AlCl <sub>3</sub> Condensers	3,500	1,320			
Leaching	290	290			
Resublimation	8,033	8,033			
CrCl <sub>3</sub> Condensers	1,415	1,415	970		
CrCl <sub>3</sub> Production				67	124
CrCl <sub>3</sub> Recovery				143	584
Cr(OH) <sub>3</sub> Recovery				268	
CrCl <sub>2</sub> Production	190	190	190		
FeCl <sub>2</sub> Production	50	50	50	100	100
MgCl <sub>2</sub> Production	362	362			
Na <sub>2</sub> CO <sub>3</sub> Recovery				416	
NaCl Recovery					522
Chlorine Handling	4,943	4,943	1,885		
Product Storages	447	447	435	577	577
Refuse and Purge Handling				985	985
Dust Control, Hygiene, Etc.	1,770	1,770	1,770	1,770	1,770
Unanticipated	5,400	6,260	1,814	3,552	443
<b>Auxiliary Equipment</b>					
Pumps, Piping & Ducts	30,000	23,795	7,000	7,620	8,270
Foundations & Supports	13,000	7,800	2,500	2,900	2,700
Power Wiring	6,500	4,000	1,500	1,250	1,350
Instrumentation	13,000	7,800	2,500	2,500	2,700
Paint & Installation	6,500	4,000	1,500	1,250	1,300
Utilities and Offsites	39,000	28,340	8,300	13,520	8,600
Engineering and Construction	67,000	52,620	14,200	25,120	15,980
Contractors Fees	9,000	5,020	1,900	2,400	1,520
Contingency	<u>17,000</u>	<u>18,220</u>	<u>3,600</u>	<u>8,700</u>	<u>5,540</u>
<b>Total Fixed Capital</b>	<b>259,950</b>	<b>190,000</b>	<b>57,000</b>	<b>97,000</b>	<b>61,500</b>
Working Capital	5,000	5,000	5,000	5,000	5,000
Cost of Technology (R&D)	<u>10,000</u>	<u>10,000</u>	<u>10,000</u>	<u>7,500</u>	<u>5,000</u>
<b>Total Investment</b>	<b>274,950</b>	<b>205,000</b>	<b>72,000</b>	<b>109,500</b>	<b>71,500</b>

TABLE IV  
ANNUAL OPERATING COSTS FOR MANUFACTURE OF REDOX CHEMICALS  
(69000 METRIC TONS/YEAR  $\text{CrCl}_3$ , 54000 METRIC TONS/YEAR  $\text{FeCl}_2$ )  
(k\$, 1981)

Manufacturing Process	Reductive Chlorination of Chrome Ore		Chlorination of Pre-Reduced Ore	Electrolytic Reduction of Sodium Chromate	Methanol Reduction of Sodium Chromate
	1 atm	3 atm		2000 A/m <sup>2</sup>	
Operating Conditions					
Manufacturing Costs					
Raw Materials					
Grade B Ore (\$81/ton)	7,300	7,300	7,300	7,830	8,100
Coke (\$85/ton)	5,993	5,933	6,660		
$\text{Na}_2\text{CO}_3$ (\$125/ton)				2,640	8,740
Lime (\$40/ton)				600	600
Chlorine (\$125/ton)	16,550	16,550	10,600		
HCl (\$75/net ton)				7,220	9,720
Iron (\$100/ton)	860	860	860	2,600	2,600
Methanol (75¢/gal)					3,600
$\text{CO}_2$ (\$64/ton)				1,350	
Other	500	500	300	100	200
Fuel and Utilities					
Electricity (35 mills)	1,420	1,420	1,420	12,120	1,800
Fuel Oil (80¢/gal)				9,336	9,700
Cooling Water	300	300	300		
Operating Labor (\$30K/man yr)					
Operating Labor	3,900	3,900	3,900	3,900	3,000
Direct Supervision (20% of OL)	780	780	780	780	600
Overheads (40% of OL)	1,900	1,900	1,900	1,900	1,500
Maintenance	10,000	7,600	2,900	4,900	3,100
Depreciation	26,000	19,000	5,700	9,700	6,150
Taxes and Insurance	4,000	2,850	1,500	2,500	1,550
Total Manufacturing Cost	79,503	68,953	44,120	67,476	60,960
Expense (Admin., etc)	3,000	3,000	2,800	2,700	2,700
Carrying Charges, Working Capital	500	500	500	500	500
Credits (sale of byproducts)					
$\text{AlCl}_3$	28,200	28,200			
$\text{MgCl}_2$	5,100	5,100			
Net Costs and Expenses	49,703	39,153	47,420	70,676	64,160



TABLE V  
ANNUAL CHARGES FOR MANUFACTURE OF REDOX CHEMICALS, CHROMIC  
CHLORIDE AND FERROUS CHLORIDE (BASIS 69000 METRIC TONS/YEAR  
ANHYDROUS CrCl<sub>3</sub> AND 54000 METRIC TONS/YEAR FeCl<sub>2</sub>)  
(k\$, 1981)

Manufacturing Process	Reduction Chlorination of Chrome Ore		Chlorination of Pre- Reduced Ore	Electrolytic Reduction of Sodium Chromate	Methanol Reduction of Sodium Chromate
	1 atm	3 atm		2000 A/m <sup>2</sup>	
<u>Venture Capital Financing</u>					
Net Costs and Expense	49,703	39,153	47,420	70,676	64,160
Less Carrying Charges	500	500	500	500	500
30% Pretax ROI	<u>82,485</u>	<u>61,500</u>	<u>21,600</u>	<u>32,900</u>	<u>21,500</u>
Total Annual Charges	131,688	100,153	68,520	103,076	85,160
Selling Price CrCl <sub>3</sub> /FeCl <sub>2</sub> , as \$/kg anhydrous CrCl <sub>3</sub>	1.91	1.45	0.99	1.49	1.23
<u>Guaranteed Return Financing</u>					
Net Costs and Expense	49,703	39,153	47,420	70,676	64,160
Less Depreciation	26,000	19,000	5,700	9,700	6,150
Amortization (10 yrs @ 10%)	<u>43,900</u>	<u>32,600</u>	<u>10,900</u>	<u>17,000</u>	<u>10,850</u>
Total Annual Charges	67,603	52,753	52,620	77,976	68,860
Selling Price CrCl <sub>3</sub> /FeCl <sub>2</sub> , as \$/kg anhydrous CrCl <sub>3</sub>	0.98	0.76	0.76	1.13	1.00

Assumptions used in calculating storage costs were the same as in the United Technology Corporation cost projections (Ref. 2) except that the costs are based on initial storage capacity before diffusional cross-over losses through the membrane which are expected to occur slowly over years of REDOX system operation. Assumptions were the following:

Discharge potential, average:	0.9 V
Depth of discharge range:	80%
Capacity loss from cross-over:	0% initially
REDOX solution compositions:	
Solar, 10 kW/500 kWh	1 molar $\text{CrCl}_3/2$ molar HCl 1 molar $\text{FeCl}_2/2$ molar HCl
Utility, 10 MW/100 MWh	2 molar $\text{CrCl}_3/2$ molar HCl 2 molar $\text{CrCl}_3/2$ molar HCl
Gross/net storage capacity:	
Solar, 10 kW/500 kWh	674/634 kWh/kWh
Utility, 10 MW/100 MWh	128/125 MWh/MWh

Additional REDOX chemicals could be added to the storage system from time to time to make up for cross-over and other losses rather than being initially charged to the system. Make-up chemicals would be part of the system operating costs.

Purchase price of hydrochloric acid was the same as used in the present manufacturing cost estimates, i.e., \$82.60/metric ton, 100% basis. This price corresponds to energy storage costs for HCl of only \$0.44/kWh and \$0.21/kWh for the solar and utility size batteries, respectively. The United Technologies projections were more than ten times higher at \$7.18 and \$3.43/kWh, respectively.

Additionally, the United Technologies study assumed a cost for ferric chloride of \$5/kWh, whereas in the present study the cost of the iron chloride is combined with the chromic chloride cost (Tables I and II). The costs are combined because the chemicals are coproducts from two of the manufacturing processes.

The Allied Chemical Project Team recommended, and subsequently undertook, Task 2, Expanded Manufacturing Cost Estimate, for the process of methanol reduction of sodium chromate. Although this process is projected to yield the second lowest price for REDOX chemicals (chlorination of prereduced ore is lowest), the process is believed to be the best defined technically of all the processes. It has the greatest probability for development to commercial success. Most of this process, production of sodium chromate yellow liquor, would utilize established commercial production technology. The rest of the process, conversion of sodium chromate yellow liquor to chromic

chloride, has been partially verified in the laboratory and is projected to involve only a few simple unit processes on a production scale. A relatively modest development effort is believed necessary to achieve commercialization. Full verification on a pilot scale would be the next phase of development.

RESULTS AND DISCUSSION OF TASK 2  
EXPANDED MANUFACTURING COST ESTIMATE

The objective of Task 2 was to refine and expand the manufacturing cost estimate of the process for methanol reduction of sodium chromate.

The refined estimate was expanded from the base case plant capacity of 69000 metric tons per year to include plant capacities of 27000 and 138000 metric tons per year of chromic chloride, anhydrous basis. A cost sensitivity analysis was then developed for the refined base case on variation in fixed capital, raw materials, and fuel oil. Finally, a flow sheet was prepared with mass balances, and a list was made of the major equipment items including specifications for sizes, ratings and materials of construction.

Results of the refined estimate of fixed capital, expanded to include the three plant capacities, were the following:

Plant Capacity Metric Tons/year $\text{CrCl}_3$	Price of Chromic Chloride and Ferrous Chloride Expressed as \$/kg $\text{CrCl}_3$
27000	1.68
69000	1.26
138000	1.10

The results substantiate the attractive price estimate obtained in the preliminary comparison. The small increase in price for the base-case capacity to \$1.26/kg from \$1.23/kg estimated in the preliminary comparison owes mainly to capital for a distillation unit for methanol recovery which was not included in the original analysis.

Results of the cost sensitivity analysis are shown in Table VI. A 25 percent increase in cost of fixed capital, raw materials and fuel oil would have a combined impact of increasing the selling price by 21 percent to \$1.53/kg. Effects of increasing costs of individual raw materials and fuel oil are minor. Selling price is particularly insensitive to the cost of methanol. A 25 percent increase in cost of methanol increases the selling price by only 0.01 \$/kg.

TABLE VI

Effect of 25 Percent Increase in Cost Element on  
Selling Price of Chromic Chloride and Ferrous Chloride  
(From Base-Case Selling Price of \$1.26/kg CrCl<sub>3</sub>)

Cost Element	Selling Price of Chromic Chloride and Ferrous Chloride, Expressed as \$/kg CrCl <sub>3</sub>	Percent Increase in Selling Price
Fixed Capital	1.37	8.73
Raw Materials		
Grade B Ore	1.29	2.32
Soda Ash	1.29	2.51
Methanol	1.27	0.54
Hydrogen Chloride	1.30	2.79
Iron	1.27	0.75
Fuel Oil	1.30	3.17
Combined Effect	1.52	20.81

Sensitivity of selling price to variations in item costs can be expressed as a linear relationship:

$$\text{Selling price (\$/kg)} = 1.26 + S \times (\% \text{ change in item cost}),$$

$$\begin{aligned} \text{where } S &= 0.00451 \text{ \$/kg}\cdot\% \text{ for fixed capital cost} \\ &= 0.00461 \text{ \$/kg}\cdot\% \text{ for total raw materials} \\ &= 0.00167 \text{ \$/kg}\cdot\% \text{ for fuel oil} \end{aligned}$$

For example, a 25 percent increase in fixed capital would require a selling price increase to \$1.37/kg in order to maintain the same rate of return and other capital related charges calculated as follows:

$$\begin{aligned} \text{Selling price} &= 1.26 + 0.00451 \times 25 \\ &= \$1.37/\text{kg} \end{aligned}$$

Annual operating charges and derived selling prices for the three plant capacities are given in Table VII.

Total Fixed Capital and investment for the three plant sizes are given in Table VIII.

Installed costs for the major capital equipment items are summarized in Table IX. The listing is the result of costing over 150 individual equipment items for each plant size.

The complete flow sheet with mass balances for the base case 69000 metric ton/year plant is given in Figure 5.

Finally, a listing of the major equipment items and their descriptions and specifications is given in Table X.

TABLE VII

Price and Annual Charges for Manufacture of Redox Chemicals  
 Chromic Chloride and Ferrous Chloride by Methanol Reduction  
 of Sodium Chromate for Three Plant Capacities  
 (k\$, 1981)

Plant Capacity (Metric tons CrCl <sub>3</sub> /yr.)	<u>27,600</u>	<u>69,000</u>	<u>138,000</u>
Fixed Capital (FC)	40,700	65,500	95,400
Manufacturing Costs			
Raw Materials			
Grade B Ore (\$81/ton)	3,240	8,100	16,200
Na <sub>2</sub> CO <sub>3</sub> (\$125/ton)	3,500	8,740	17,480
Lime (\$40/ton)	250	600	1,200
Methanol (75¢/gal)	750	1,870	3,740
HCl (\$75/ton)	3,900	9,720	19,440
Iron (\$100/ton)	1,040	2,600	5,200
Other	100	200	400
Fuel and Utilities			
Electricity (\$0.035/kWh)	720	1,800	3,600
Fuel Oil (80¢/gal.)	4,600	11,500	23,000
Operating Labor (OL) (\$30k/man yr)	2,700	3,000	4,800
Direct Supervision (20% of OL)	540	600	960
Overheads (40% of OL)	1,350	1,500	2,300
Maintenance (5% of FC)	2,040	3,300	4,770
Depreciation (10% of FC)	4,070	6,600	9,540
Taxes and Insurance (2.5% of FC)	<u>1,020</u>	<u>1,650</u>	<u>2,390</u>
Total Manufacturing Cost	29,820	61,780	115,020
Expense (Admin. etc.)	2,000	2,700	3,500
Return on Investment (30%)	<u>14,610</u>	<u>22,650</u>	<u>33,120</u>
Total Annual Charges	46,430	87,130	151,640
Selling Price (\$/kg CrCl <sub>3</sub> , inc. FeCl <sub>2</sub> )	1.68	1.26	1.10

TABLE VIII

Fixed Capital and Total Investment for Three Plant  
 Sizes Producing Redox Chemicals by Methanol Reduction  
 of Sodium Chromate  
 (k\$, 1981)

Plant Capacity (Metric tons, CrCl <sub>3</sub> /yr.)	<u>27,600</u>	<u>69,000</u>	<u>138,000</u>
Fixed Capital			
Major Equipment	8,850	14,300	20,800
Auxiliary Equipment			
Piping, Chutes, Ducts	5,300	8,600	12,500
Foundations, Supports	1,800	2,850	4,200
Power Wiring	900	1,450	2,100
Instruments, Controls	1,800	2,850	4,200
Insulation, Paint	<u>900</u>	<u>1,450</u>	<u>2,100</u>
Total Direct Equipment	19,550	31,500	45,900
Utilities and Offsites	5,900	9,450	13,800
Engineering and Construction Contractor Fees	10,200 1,500	16,400 2,100	23,900 3,100
Contingency	<u>3,750</u>	<u>5,950</u>	<u>8,700</u>
Total Fixed Capital	40,700	65,500	95,400
Working Capital	3,000	5,000	10,000
Cost of Technology	<u>5,000</u>	<u>5,000</u>	<u>5,000</u>
Total Investment	40,700	75,500	110,400

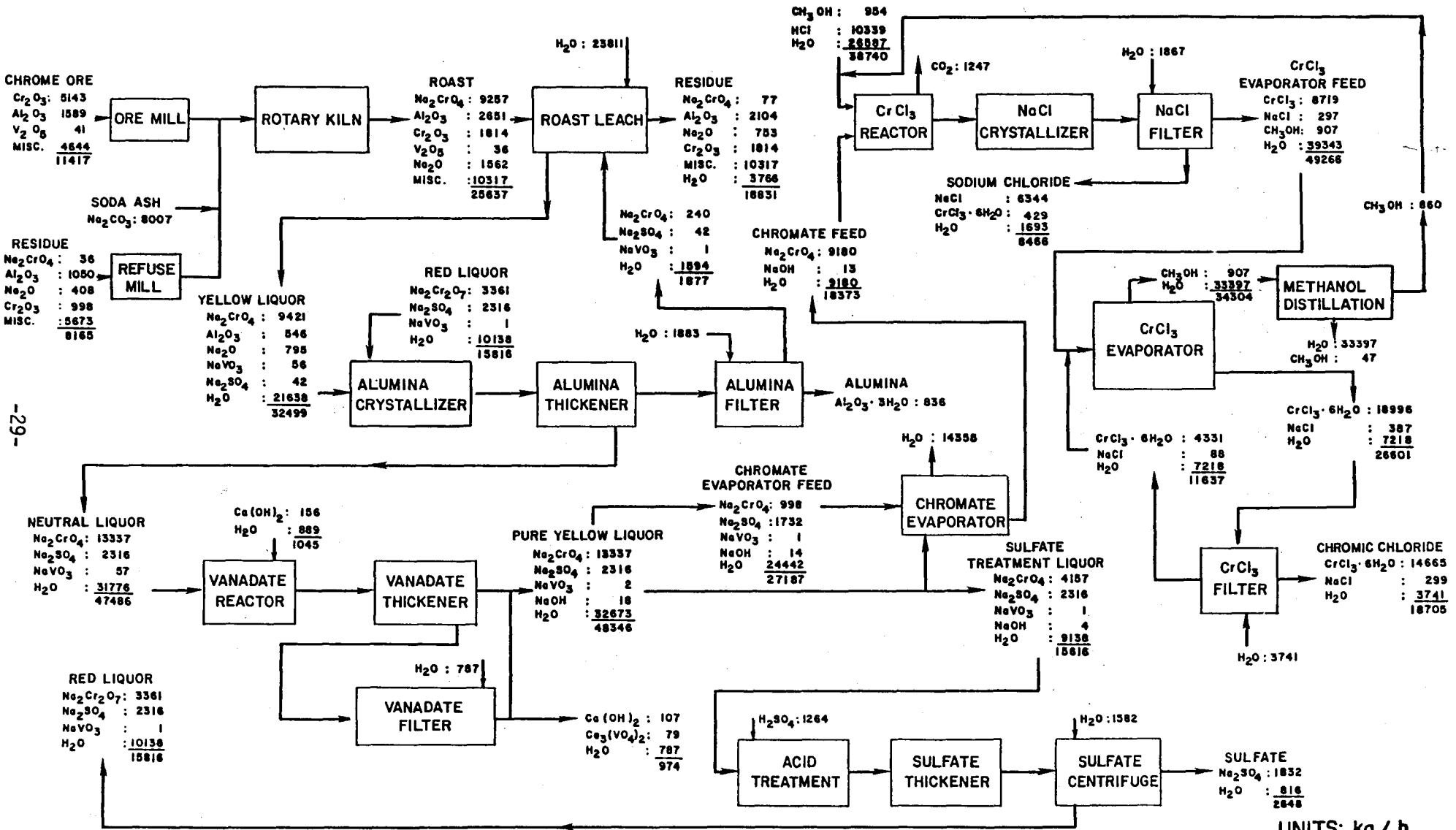


TABLE IX  
 Major Capital Equipment Installed  
 (Summary of 150 item costs for each plant capacity)  
 (1981 \$)

Plant Capacity (Metric tons, CrCl <sub>3</sub> /yr.)	<u>27,600</u>	<u>69,000</u>	<u>138,000</u>
Major Equipment			
Ore Handling	523,300	906,000	1,377,500
Refuse Handling	381,200	592,000	838,100
Soda Ash Handling	108,100	187,000	284,500
Mixing	114,600	198,000	301,200
Roasting	1,911,800	2,530,000	3,135,700
Leaching	253,900	440,000	668,800
Alumina Recovery	430,400	745,000	1,132,700
Vanadium Removal	234,100	404,700	615,800
Finishing	189,300	327,000	498,000
Sulfate Handling	180,100	292,000	426,800
Concentration	380,400	658,000	1,000,500
CrCl <sub>3</sub> Production	1,487,100	2,446,400	3,585,900
FeCl <sub>2</sub> Production	341,400	591,000	898,700
Miscellaneous	2,067,500	3,583,000	5,434,300
Storage			
Hygiene			
Refuse Treatment			
Methanol Recovery			
Unanticipated	<u>246,800</u>	<u>399,900</u>	<u>601,500</u>
Total Major Equipment	8,850,000	14,300,000	20,800,000

FIGURE 5

MATERIAL BALANCE PROCESS SCHEME FOR METHANOL REDUCTION OF SODIUM CHROMATE



UNITS: kg / h

TABLE X

MAJOR EQUIPMENT ITEMS FOR PLANT PRODUCING  
69000 METRIC TONS PER YEAR  $\text{CrCl}_3$  (ANHYDROUS BASIS)  
BY METHANOL REDUCTION OF SODIUM CHROMATE

<u>Equipment</u>	<u>Description and Specifications</u>
Ore Mill System	Williams Super Giant Roller Mill, complete with cyclone and bag dust collectors.
Refuse Mill System	William Champion Roller Mill, complete with cyclone and bag dust collectors.
Rotary Kiln System	13' diameter x 300' long rotary kiln lined with A.P. Green DV-38 brick, complete with gas burner, drive, controls, exhaust gas and inlet air blowers, etc.
Leach Filters	Dorr-Oliver belt filter, complete with filtrate receivers and pumps, and vacuum pump, plus polish filters.
Alumina Crystallizers	Three 30000-gallon vertical steel tanks with 30 HP agitators and 200 ft <sup>2</sup> steam coils.
Alumina Thickener	Rake-type thickener, 38 ft dia x 10 ft deep, steel.
Alumina Filter	Rotary vacuum filter, 6 ft dia x 14 ft wide, steel, complete with filtrate receivers, filtrate pumps and vacuum pumps.
Vanadate Reactors	6500 gallon vertical steel tank, 10 HP agitator.
Vanadate Thickener	Rake-type thickener, 40 ft dia x 10 ft deep, steel.

TABLE X  
(Continued)

MAJOR EQUIPMENT ITEMS FOR PLANT PRODUCING  
69000 METRIC TONS PER YEAR  $\text{CrCl}_3$  (ANHYDROUS BASIS)  
BY METHANOL REDUCTION OF SODIUM CHROMATE

<u>Equipment</u>	<u>Description and Specifications</u>
Vanadate Filter	Rotary vacuum filter, 5 ft dia x 8 ft wide, steel, complete with filtrate receiver, filtrate pump and vacuum pump.
Chromate Evaporator System	Quadruple effect evaporator train, Oslo crystallizing type, steel, complete with vaporizers, suspension tanks, heater, circulating pumps, liquor transfer pumps, salt legs, water pumps, barometric condenser and ejector, condensate and flash tanks, hot well, etc.
Treating Tanks	Two 5000 gallon vertical steel tanks with 45° cone bottoms and 5 HP agitators.
Sulfate Thickeners	Two 2000 gallon steel, cone-bottom tanks with 6" variable-speed vertical screw dischargers with 5 HP drives.
Sulfate Centrifuges	Two TerMeer centrifugal separators, steel, with 20 HP drives.
Chromic Chloride Reactors	Two 7000 gallon, rubber-lined steel tanks, with internal heating coil and 12 HP agitator.
Sodium Chloride Crystallizers	Two 7000 gallon, rubber-lined steel tanks, with internal cooling coil and 12 HP agitator.

TABLE X  
(Continued)

MAJOR EQUIPMENT ITEMS FOR PLANT PRODUCING  
69000 METRIC TONS PER YEAR  $\text{CrCl}_3$  (ANHYDROUS BASIS)  
BY METHANOL REDUCTION OF SODIUM CHROMATE

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<u>Equipment</u>	<u>Description and Specifications</u>
Sodium Chloride Filter	Rotary vacuum filter, 4 ft dia x 8 ft wide, rubber lined steel, complete with filtrate receivers, filtrate pumps and vacuum pumps.
Chromic Chloride Evaporative System	Quadruple effect evaporator train, Oslo crystallizing type, monel clad steel, complete with vaporizers, suspension tanks, heaters, circulating pumps, liquor transfer pumps, salt legs, water pumps, barometric condenser and ejector, condensate and flash tanks, hot well, etc.
Methanol Recovery	Distillation unit. 304 SS complete with packed column, condenser, and reboiler.
Chromic Chloride Filter	Rotary vacuum filter 5 ft dia x 9 ft wide, rubber lined steel, complete with filtrate receivers, filtrate pumps and vacuum pumps.

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## CONCLUSIONS

The cost study showed the economic feasibility of producing REDOX chemicals on a commodity chemical scale for profitable sale at a cost-effective price for the NASA REDOX Energy Storage System. Two potentially attractive processes were identified, methanol reduction of sodium chromate and chlorination of prereduced chrome ore. The methanol process is of greater immediate interest even though the other process may be potentially less costly, because its technical details are more completely understood and it should be more easily developed into a commercial process. Furthermore, the methanol process would have the versatility with minor modification of producing other commercially important chrome chemicals as well.

The projected selling price of REDOX chemicals by the methanol process, \$1.26/kg  $\text{CrCl}_3$ , including  $\text{FeCl}_2$ , corresponds to a specific energy storage cost of \$11/kWh. Projected storage cost for chemicals produced by the reductive chlorination process is under \$9/kWh. These results support the NASA REDOX system as a potentially economically feasible device for utility and other bulk storage applications.

Cost sensitivity analysis conducted on the methanol process showed that the price of REDOX chemicals by this process would be relatively little affected by changes in costs of individual raw materials and fuel. The process is capital intensive, but less so than the other processes, and a 25% change in capital costs would cause a 7% change in REDOX chemical price.

The scale of operation had a typical effect on selling price, ranging from \$1.10/kg to \$1.68/kg when the plant capacity decreased from 138000 metric tons  $\text{CrCl}_3$  per year to 27600 tons per year.

## REFERENCES

1. Thaller, L. H., "Recent Advances in Redox Flow Cell Storage Systems". Proceedings of the Fourteenth Intersociety Energy Conversion Engineering Conference, August 5-10, 1979; and private communications.
2. "Cost Projections for Redox Energy Storage Systems", Final Report. NASA CR-165260. NASA contract DEN3-126. Power Systems Division, United Technologies Corporation, February 1980.
3. Boericke, F.S. and Bangert, W.M., "Effect of Variables in Chemical Benefication of Chromite Ores". U.S. Bureau of Mines, R.I. 3817, July, 1945.

1. Report No. NASA CR-167881		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle Study to Establish Cost Projections for Production of Redox Chemicals				5. Report Date November 1982	
				6. Performing Organization Code 776-72-41	
7. Author(s) J. F. Walther, C. C. Greco, R. N. Rusinko, and A. L. Wadsworth, 3rd				8. Performing Organization Report No.	
				10. Work Unit No.	
9. Performing Organization Name and Address Syracuse Research Laboratory Allied Chemical Company P.O. Box 6 Solvay, New York 13209				11. Contract or Grant No. DEN 3-250	
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				15. Supplementary Notes Final Report. Prepared under Interagency Agreement DE-AI04-80AL12726. Project Manager, R. F. Gahn, Solar and Electrochemistry Division, NASA Lewis Research Center, Cleveland, Ohio 44135.	
16. Abstract A cost study of four proposed manufacturing processes for redox chemicals for the NASA REDOX Energy Storage System yielded favorable selling prices in the range \$0.99 to \$1.91/kg of chromic chloride, anhydrous basis, including ferrous chloride. The prices corresponded to specific energy storage costs from under \$9 to \$17/kWh. A refined and expanded cost analysis of the most favored process yielded a price estimate corresponding to a storage cost of \$11/kWh. The findings supported the potential economic viability of the NASA REDOX system.					
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