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The Economics of Salt Cake Recycling *

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Introduction

Aluminum recycling is critical to the sustainability of the aluminum industry because of the resources it conserves, particularly energy and bauxite ore. The large volume of waste (dross and salt cake) generated during aluminum recycling poses a potential threat to the secondary aluminum industry. These wastes are typically disposed of in landfills. As the costs of landfilling increase and the availability of landfill space decreases, disposal of these residues will increasingly compromise the economics of aluminum recycling. Argonne National Laboratory, in cooperation with the U.S. Department of Energy and the Aluminum Recycling Association, has undertaken to develop technology for the recovery of aluminum, salt fluxes, and aluminum oxide from the residues generated during aluminum recycling.

The initial emphasis of this program has been to evaluate alternative technologies for salt cake recycling. Salt cake is generated in rotary furnaces from the melting of low-grade aluminum scrap, including black dross. An estimated 460,000 metric tons of salt cake are generated annually in the United States. The aluminum content of salt cake is typically lower than that of black dross, reducing the profitability of additional aluminum extraction. The composition of salt cake varies with its origins, comprising 5-7 wt% aluminum, 10-50 wt% salts, and 50-85 wt% residue-oxide, which consists primarily of aluminum oxide with minor amounts of cryolite, magnesium oxide, magnesium aluminate, and other contaminants.

In this paper, results are presented from a preliminary economic assessment of four potential salt-cake-recycling technologies:

- *base case process:* leaching in water at 25°C, with evaporation to crystallize salts;

- *high-temperature process:* leaching in water at 250°C, with flash crystallization to precipitate salts;
- *solvent/antisolvent process:* leaching in water at 25°C, with precipitation of salts by acetone addition; and
- *electrodialysis process:* leaching in water at 25°C, with concentration and recovery of salts by electrodialysis.

Sensitivities to the cost of landfill disposal and by-product value were evaluated. The results of the economic analyses have helped to define future directions for the development of salt-cake-recycling technology.

Alternative Technologies for Salt Cake Recycling

At present, salt cake residues generated from domestic aluminum recycling are almost exclusively landfilled. We are aware of only three facilities in the United States that commercially recycle salt cakes: Aluminum Waste Technology (Cleveland, Ohio), Reynolds Metals Company (Richmond, Virginia), and Imsamet (Litchfield Park, Arizona). In Europe, landfill restrictions have compelled more companies to employ salt cake recycling. Several European companies are offering process licenses for salt-cake-recycling systems, including Engitec Impianti S.pA. of Italy, Berzelius Umwelt-Service A.G. (B.U.S) of Germany, and Sulzer Escher Wyss of Switzerland. The base case process option evaluated in this study is representative of these commercial processes. The other three process alternatives have not been commercialized or piloted.

Block diagrams of the four salt-cake-recycling processes evaluated are provided in Figures 1-4. The process objectives and equipment in the solids preparation, gas treatment, and product recovery sections of each of the recycling options are the same. In the solids preparation section, the salt cake is dry-crushed, screened, and magnetically separated to recover an aluminum-rich, iron-free by-product for remelting in a secondary aluminum furnace. We assumed that 70% of the aluminum in the salt cake is recovered in this by-product stream at 50% purity. The effluent from the solids preparation section is salt cake, depleted in aluminum and crushed to less than 1-mm size, for feed to leaching.

The gas treatment section is required to control emissions of toxic and explosive gases generated when salt cake is leached in water. According to European sources,[1,2] hydrogen, ammonia, methane, phosphine, and hydrogen sulfide are emitted from the leaching reaction. In the conceptual design for all options, the gas treatment section consists of a thermal oxidizer followed by a chlorine scrubber.

In the product recovery section, the salt solids are separated from the brine solutions with a centrifuge and are then dried and stored for sale. Process steps unique to the individual recycling options are described briefly in the following subsections.

Base Case Process

The conceptual design for the base case process was derived from information about salt-cake-recovery technologies that have been commercialized, licensed, and/or developed by the following companies: B.U.S.,[1] Engitec,[2] Aluminum Waste Technology,[3] Sulzer Escher Wyss,[4] and the U. S. Bureau of Mines.[5]

In the base case process, crushed salt cake from the solids preparation section is fed to a leaching tank, where the salts are dissolved in water at ambient conditions (25°C, 1 atm) to yield a brine concentration of 22 wt% salts. Insolubles (aluminum oxide) in the leach effluent are separated from the brine and washed with water to remove residual salts. The wet oxide residue is landfilled or further processed for sale.

The clarified brine solution is fed to a forced-circulation evaporator system designed for energy recovery (single-effect with vapor recompression or multiple-effect). The NaCl and KCl salts crystallize as the water is evaporated. The slurry effluent from the evaporator is then routed to product recovery. The filtrate from the centrifuge is recycled back to the evaporator to maximize recovery of salts.

The evaporator system is the largest contributor to capital cost and energy consumption in this process option. Expensive metallurgy is required for equipment in contact with the highly corrosive hot brines. The equipment size and energy usage are driven by the amount of water that must be vaporized. The evaporation load is, in turn, dependent on the brine concentration attained in the leach reaction. In commercial operations, the leach effluent brine concentration is less than saturation. We are investigating leach reaction conditions with the goal of attaining higher brine concentrations in the leach effluent.

High-Temperature Process

Researchers at ANL[6] proposed the option of leaching the salts from salt cake at elevated temperature and pressure to yield a more concentrated brine solution than is attainable at ambient conditions. To assess this potential, we are experimentally determining the effect of temperature on the solubility of salt cake components. In lieu of the salt-cake-specific solubility data, literature data[7] were employed to derive a NaCl/KCl/water phase diagram for the preliminary design and economic evaluation of this process option.

The conceptual design employed for the preliminary economics assumes salt cake leaching at 250°C and 51 atm. The crushed salt cake from the solids preparation section is slurried with water and then heated to leaching temperature in a series of heat exchangers. The salts are dissolved in the leach reactor to a brine concentration of 40 wt%. The hot leach effluent is then processed to remove the insoluble oxide residue. The wet oxide residue is landfilled or further processed for sale.

The clarified brine is cooled and depressurized in a series of three flash crystallizers. As the water flashes and solution cools, the salts crystallize. The slurry effluent from the third crystallizer is fed to the product recovery section. The filtrate from the product centrifuge is recycled back to the leach reactor feed to maximize salt recovery.

Equipment for this process is costly because of the high-pressure design and titanium metallurgy (required to process brines at elevated temperatures). The equipment size, and hence capital cost, is largely dependent on the brine concentration achieved in the leach reactor and the per-pass recovery of salt (which defines the internal recycle volume). In turn, both of these parameters are defined by the solubility characteristics of the salt cake components, which are currently being investigated experimentally.

Solvent/Antisolvent Process

The solvent/antisolvent process has been patented by researchers at ANL[8] as an alternative to evaporation. The process concept relies on the ability to precipitate a solute from a solvent by the use of another solvent. Results of preliminary laboratory tests identified acetone as an effective antisolvent for precipitating salts from a brine solution. In additional tests, the effectiveness of acetone in precipitating salts was found to be severely reduced if the salt concentration in the feed was not at or near saturation. Hence, some pre-evaporation of the feed from the leach reaction was found to be necessary. A material/energy balance and a conceptual design for the process were derived from these laboratory tests.

As in the base case process, crushed salt cake from the solids preparation section is fed to a leaching tank, where the salts are dissolved in water at ambient conditions (25°C, 1 atm) to yield a brine concentration of 22 wt% salts. Insolubles (aluminum oxide) in the leach effluent are separated from the brine and washed with water to remove residual salts. The wet oxide residue is landfilled or further processed for sale.

The clarified brine solution is fed to a forced-circulation evaporator system designed for energy recovery (single-effect with vapor recompression or multiple-effect). In the evaporator, the brine is concentrated to saturation. The evaporator system is smaller than that required in the base case process.

The saturated brine and recycle streams are then fed to the antisolvent reactor with acetone at a rate that will render an acetone/water volume ratio of 1/1. After vigorous mixing in the reactor, the combined stream is fed to a decanter, where three effluent streams are generated through settling: (1) an upper cut stream - supernatant liquid containing a mixture of approximately 85 wt% acetone and 15 wt% water; (2) a middle cut stream - liquid containing water with dissolved salts (~28 wt%) and acetone (~20 wt%); and (3) a bottom cut stream - slurry containing settled salt precipitates (~25 wt%) in water with dissolved salts and acetone.

The supernatant stream is routed to a distillation tower for separation from water and recycling of the acetone. The middle cut stream is recycled back to the antisolvent reactor, and the bottom cut stream is fed to the product recovery section. The filtrate from the product centrifuge is recycled back to the antisolvent reactor. In laboratory experiments, acetone addition precipitated 23-24 wt% of the dissolved salts. Consequently, internal recycling is important to maximize salt recovery.

The evaporator system and acetone recovery distillation tower are the greatest contributors to capital cost and energy usage in this process concept. As with the base case process, the size, cost, and energy usage of the evaporator system depend on the brine concentration achieved in the leach reactor. For this process, the evaporator system could be eliminated completely if the brine could be concentrated to saturation in the leach reactor. The size, cost, and energy consumption of the acetone recovery tower are dictated by the internal recycle stream volume, which defines the acetone requirements to the antisolvent reactor. At the relatively low per-pass recovery of 23-24 wt% salts, this volume is significant.

Electrodialysis Process

Another alternative to evaporation identified by ANL researchers is electrodialysis (ED). For salt cake recycling, electrodialysis would be employed to transfer the salts from the leach effluent brine solution to a saturated brine solution, from which they would be precipitated for recovery. Development studies with a pilot-scale ED cell are under way for proof of concept and, ultimately, to generate design data. The preliminary material/energy balance and equipment design are based on vendor quotations.

The front-end equipment of the electrodialysis process is the same as in the base case and solvent/antisolvent processes. Crushed salt cake from the solids preparation section is fed to a leaching tank, where the salts are dissolved in water at ambient conditions (25°C, 1 atm) to yield a brine concentration of 22 wt% salts. Insolubles (aluminum oxide) in the leach effluent are separated from the brine and washed with water to remove residual salts. The wet oxide residue is landfilled or further processed for sale.

The clarified brine is then combined with the ED cell diluate stream and fed to the ED cell. Saturated brine is recycled through the system as the concentrate stream. Salts in the feed stream are transferred, via the electrical driving force, through the alternating ion exchange membranes (Cl^- through the anion exchange membrane, and Na^+ and K^+ through the cation exchange membrane) into the saturated brine concentrate stream. The salts will precipitate as the concentration increases. The effluent concentrate stream is fed to a settling tank, where the solids are concentrated by gravity. The slurry bottoms from this tank are then fed to the product recovery section. The filtrate from the product centrifuge is recycled to the ED-cell concentrate feed stream.

The ED cell is the major contributor to capital cost and energy consumption in this process concept. These two parameters are inversely related in electrodialysis. Capital cost is minimized by reducing the number of ED cells in the stack, but at the expense of increased energy usage. Because overall process economics are relatively more sensitive to capital cost, the goal of our research is to determine the smallest number of cells required to achieve salt recovery.

Economic Assessment Parameters

The economic analyses for all processes are based on a plant capacity of 30,000 metric tons of salt cake feed per year, with an operating factor of 90% (330 d/yr, 24-h/d operation). The salt cake composition is assumed to be 6 wt% aluminum, 14 wt% sodium chloride, 14 wt% potassium chloride, and 66 wt% aluminum oxide. Capital charges are calculated for a 20% return on investment. The pricing structure employed in the estimates is provided in Table I.

Table I: Pricing Structure for Economic Study of Salt Cake Recycling

Component	**Price**
Salt cake feed*	- $44/metric ton salt cake
Aluminum oxide residue landfill	$66/metric ton residue
By-product aluminum**	$1280/metric ton Al
Product salts (mixed NaCl and KCl)	$66/metric ton salts
De-ionized water	$1.1/m^3 water
Acetone	$ 820/metric ton acetone
Electricity	$ 0.06/kWh electricity
Steam	$ 11/metric ton steam
Natural gas	$ 0.11/m^3 natural gas
Labor	$17/h

* Salt cake feed cost is actually a credit, assumed to be the landfill avoidance savings less any costs to transport salt cake to the recycling facility.

** By-product aluminum value taken for aluminum content only.

Results of Economic Assessment

The results from the preliminary economic assessment of the four salt-cake-recycling options are summarized in Table II. For these estimates, we assumed the wet oxide residue is landfilled. The production cost estimates should be compared to the sales price of mixed NaCl and KCl salts, $66/metric ton. The energy consumed in the individual processes is proportional to, and hence represented by, the utilities component of the production cost.

Table II: Economic Assessment of Salt-Cake-Recycling Process Options

Economic Parameter	**Base Case Process**	**High-Temperature Process**	**Solvent/ Antisolvent Process**	**Electrodialysis Process**
Capital cost ($\$10^6$)	12.8	10.1	16.0	8.2
Net present value ($\$10^6$)	-10	-7	-15	-6
Production cost breakdown ($/metric ton salt product)				
Salt cake feed	-175	-179	-175	-175
Al fraction by-product	-214	-218	-213	-214
Al oxide residue	202	207	201	202
Chemicals	6	4	101	4
Utilities	61	67	125	68
Fixed costs	140	118	163	107
Capital charges	611	436	761	399
TOTAL	**631**	**435**	**963**	**391**

The estimates provided in Table II clearly show the solvent/antisolvent process to be the most costly and energy-intensive of all options considered. This unanticipated result is attributed to the need to pre-evaporate the brine solution and to the high acetone flows dictated by the low per-pass recovery of salts, as discussed previously. No further development of this technology will be pursued. Both the high-temperature and the electrodialysis process options, on the other hand, show the potential to offer capital savings over existing technology.

All technology options have a negative present value, given the current pricing structure and 20% return on investment. Although manufacturing costs (variable plus fixed) could be reasonably recovered in the sales price of the salt product, the capital costs cannot. Simply stated, the low value for NaCl and KCl salt mixtures ($66/metric ton) cannot support the capital investment required to recover these salts from salt cake by any of the processes evaluated. In fact, for a given technology to be profitable at 20% return, its capital cost would need to be less than $2 million.

The discovery of such a low-capital technology seems unlikely, so other strategies are being adopted to reduce costs. Specifically, we are evaluating opportunities to market the aluminum oxide residue, instead of disposing of it. The base case process would be profitable if the aluminum oxide residue could be sold for $220/metric ton. The high-temperature and electrodialysis processes would be profitable at aluminum oxide values of $115/metric ton and $101/metric ton, respectively. As landfill costs increase, the aluminum oxide value required to make the project profitable decreases as depicted in Figure 5.

The recovery of aluminum oxide for sale will, in fact, become increasingly important as landfill costs increase. For salt cakes containing high concentrations of aluminum oxide, the costs of landfilling the oxide residue cancel the savings associated with not landfilling the salt cake. If the aluminum oxide is not recovered for sale, the economics for salt cake recycling will not be favorable, even though landfill costs are higher. In just such a situation, however, the secondary aluminum industry will be most in need of salt-cake-recycling options.

The marketability of the aluminum oxide by-product will be dependent on its purity, particularly its concentration of salts and aluminum. Additional processing will likely be required to meet specifications for the selected application.

The economics of salt cake recycling can also be improved at higher capacities (>30,000 metric tons/yr), but only if the oxide residue is recovered for sale and not landfilled. The effect of capacity on the base case economics is depicted in Figure 6. As capacity increases, the oxide residue value required to make the project profitable decreases. Of course, capacity decisions are dependent on feedstock sourcing issues (i.e., the availability and transport costs for the salt cake feed).

Another possibility for improving the economics of salt cake recycling is to increase the value of the product salt. Researchers at the University of Tennessee Space Institute[9] are developing technology to convert sodium and potassium chloride salts to carbonate salts. This alternative is based on a patented anion-exchange resin process for the dechlorination of brine solutions. They claim the product from their process has a market value of $322/metric ton.

A final observation from the economic analysis relates the importance of aluminum recovery to salt cake recycling. The production costs for the recycling process would increase significantly for salt cakes with a lower aluminum content, or if the achievable aluminum recovery were less than assumed. Salt cake recycling can be made more profitable by supplementing the feed with drosses that have higher aluminum concentrations. From another perspective, our economic studies indicated that extracting only the aluminum from salt cake (i.e., landfilling the aluminum-depleted salt cake) would be profitable as long as the aluminum recovered equaled about 4-5% of the original salt cake weight.

Conclusion

The results of this preliminary economic study have charted the future direction for research on salt cake recycling at ANL. Our efforts are directed at developing less capital-intensive technology and at developing the technology and markets for the recovery of aluminum oxide from salt cake. With regard to the first endeavor, we are concentrating on electrodialysis process development. Several technical uncertainties and concerns associated with the high-temperature process have relegated it to a second-priority option.

Processes that convert the oxide content of salt cakes to value-added alumina products are necessary to the profitability of salt cake recycling. ANL is developing processes to generate products that meet specifications for ceramic fiber insulation, abrasives, and other applications.

Finally, we note that addressing the problem of salt cake at the aluminum recycling facility may yield the most profitable solutions. Research aimed at reducing the amount of salt cake generated in the aluminum remelt furnaces is being conducted by the secondary aluminum industry, and we continue to hope for a significant breakthrough.

Acknowledgment

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Figure 1: Block Diagram of Base Case Salt-Cake-Recycling Process

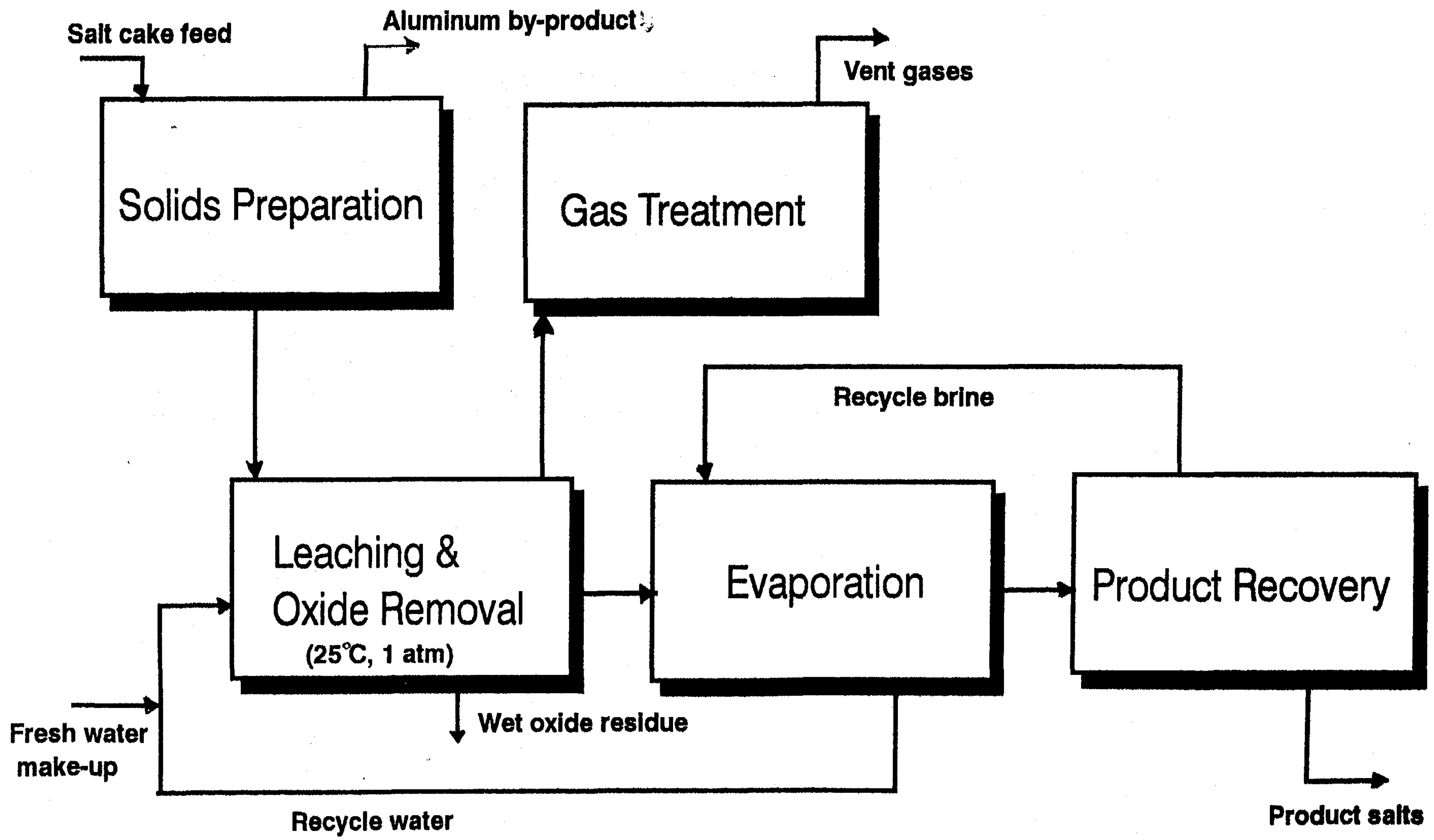


Figure 2: Block Diagram of High-Temperature Salt-Cake-Recycling Process

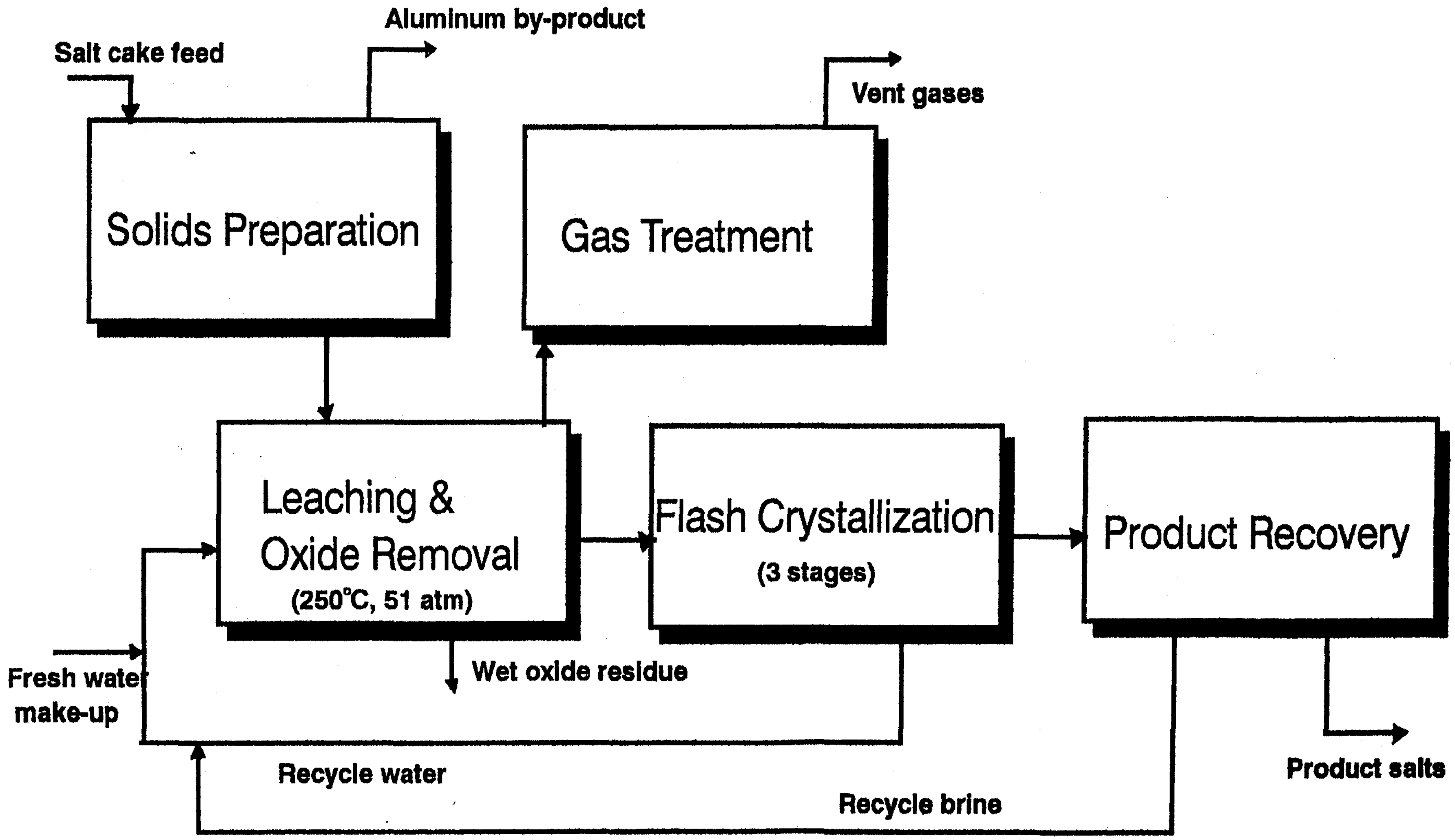


Figure 3: Block Diagram of Solvent/Antisolvent Salt-Cake-Recycling Process

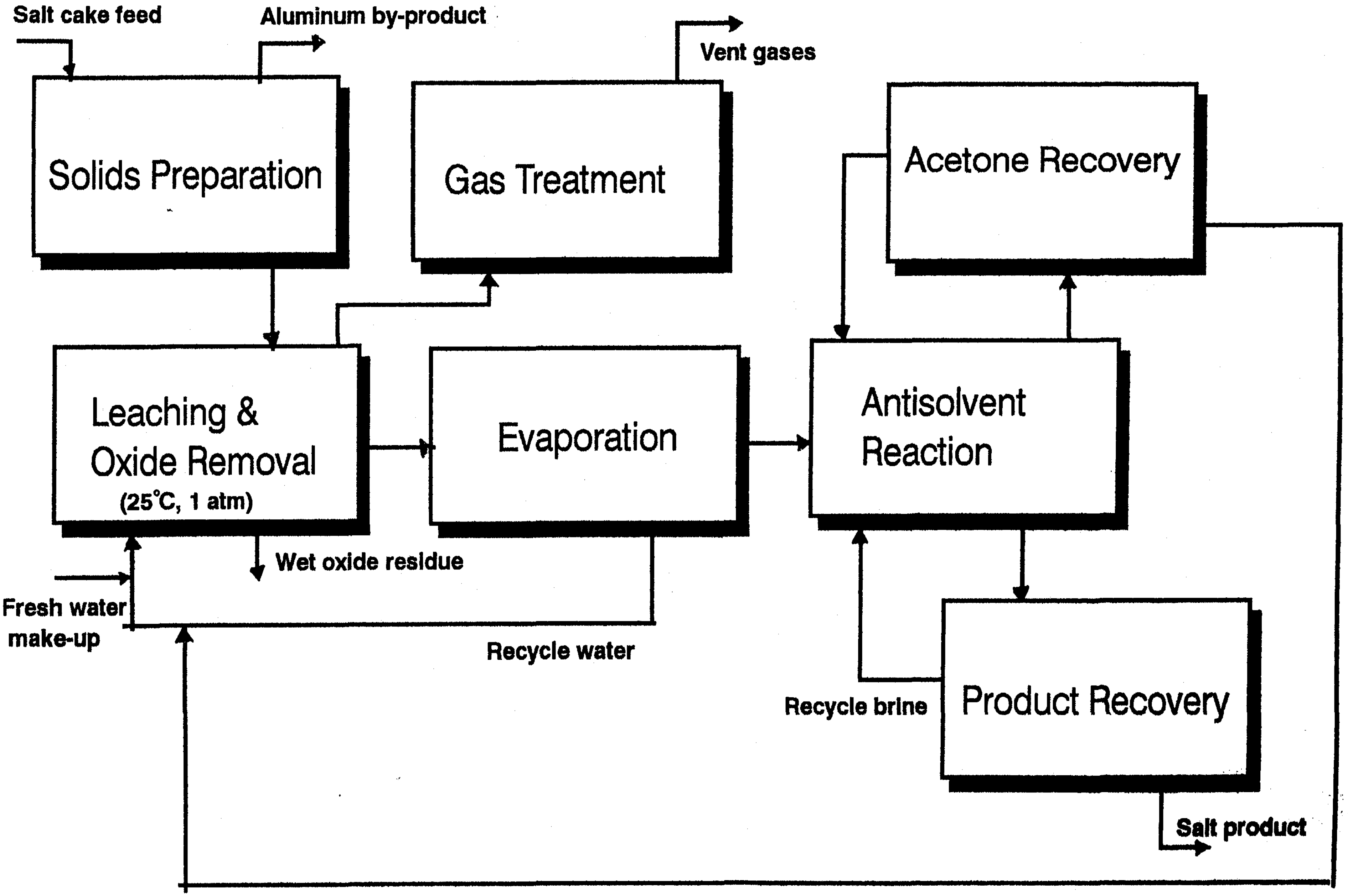


Figure 4: Block Diagram of Electrodialysis
Salt-Cake-Recycling Process

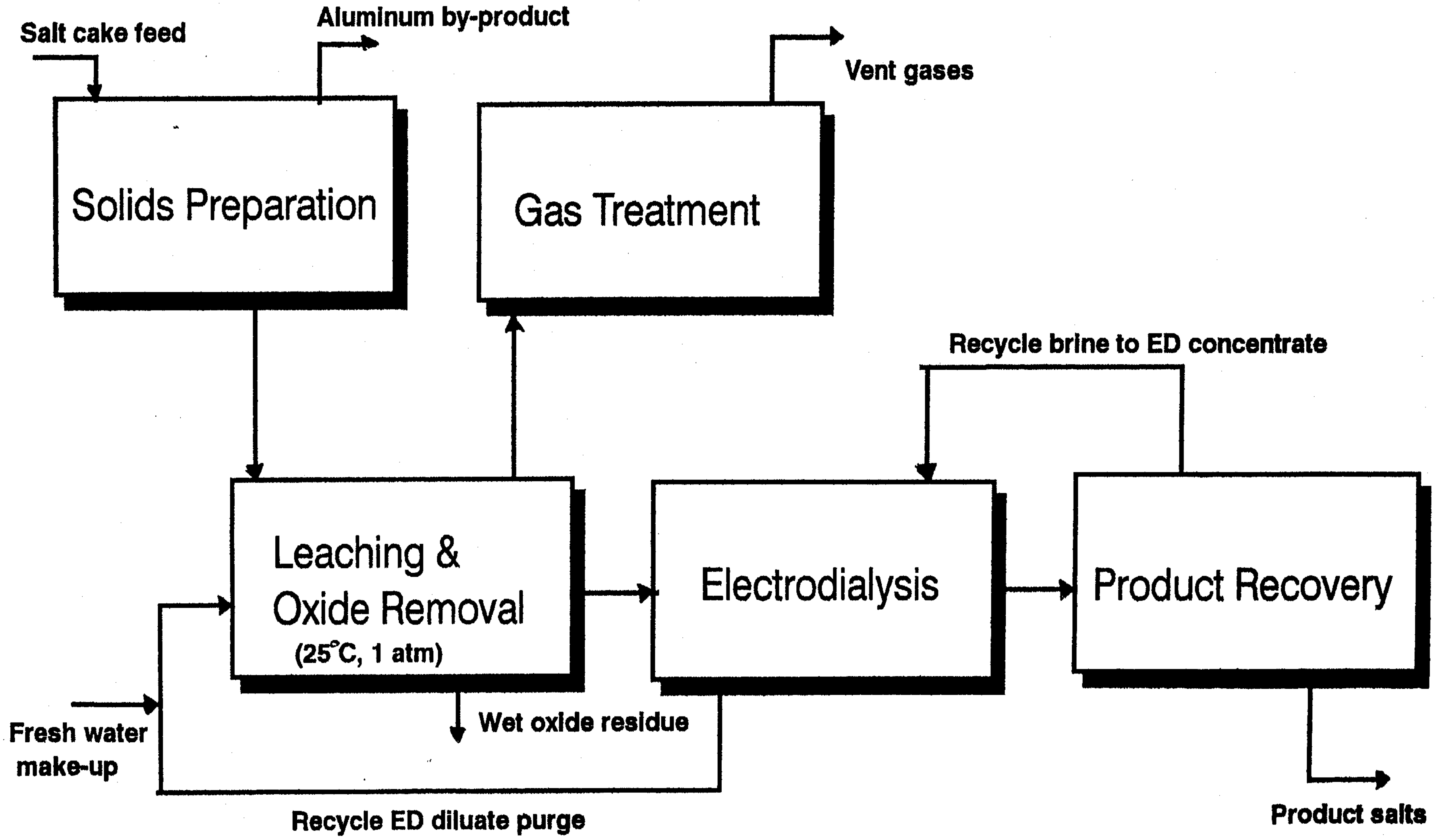


Figure 5: Effect of Landfill Cost on Required Al Oxide Residue Value

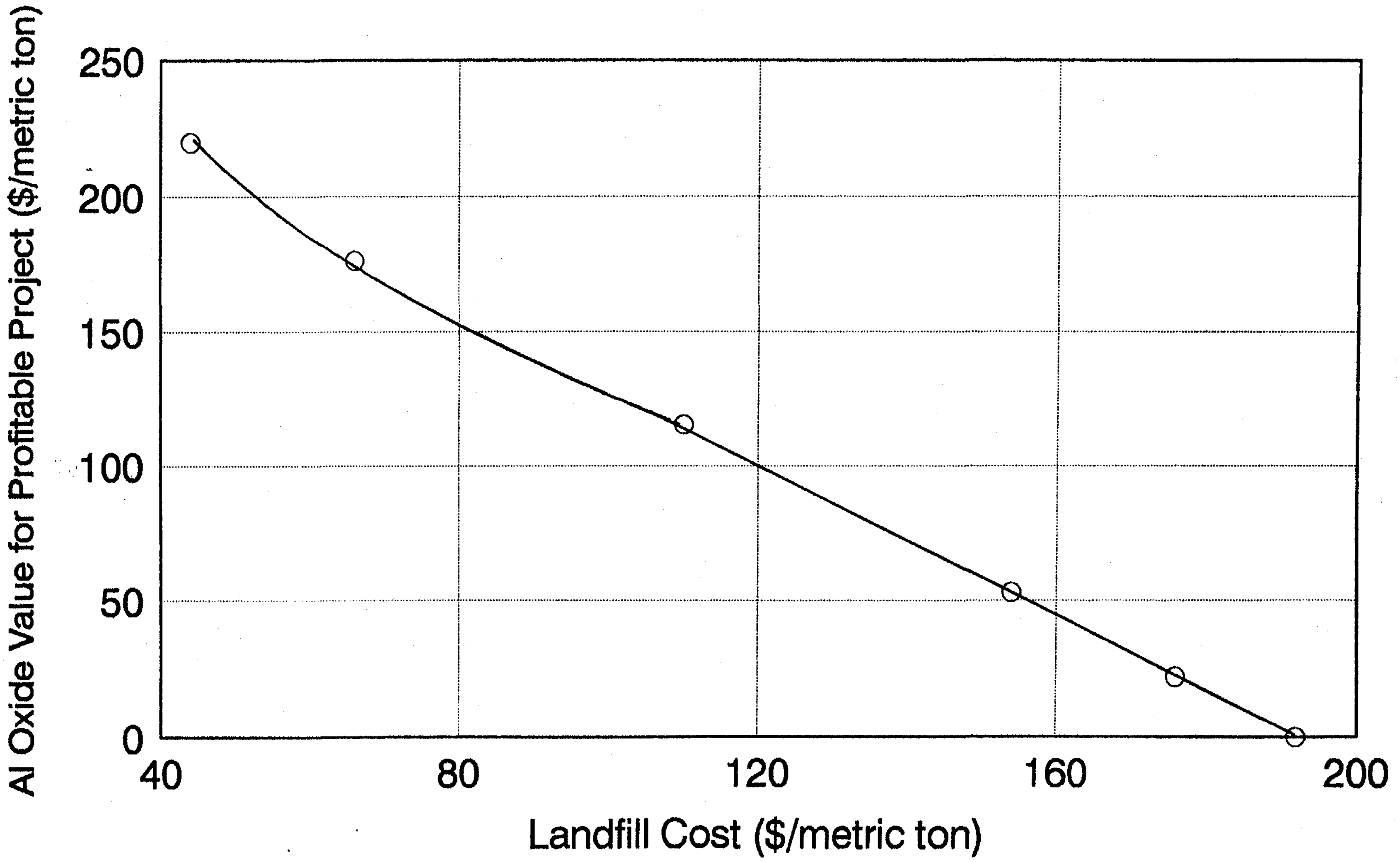
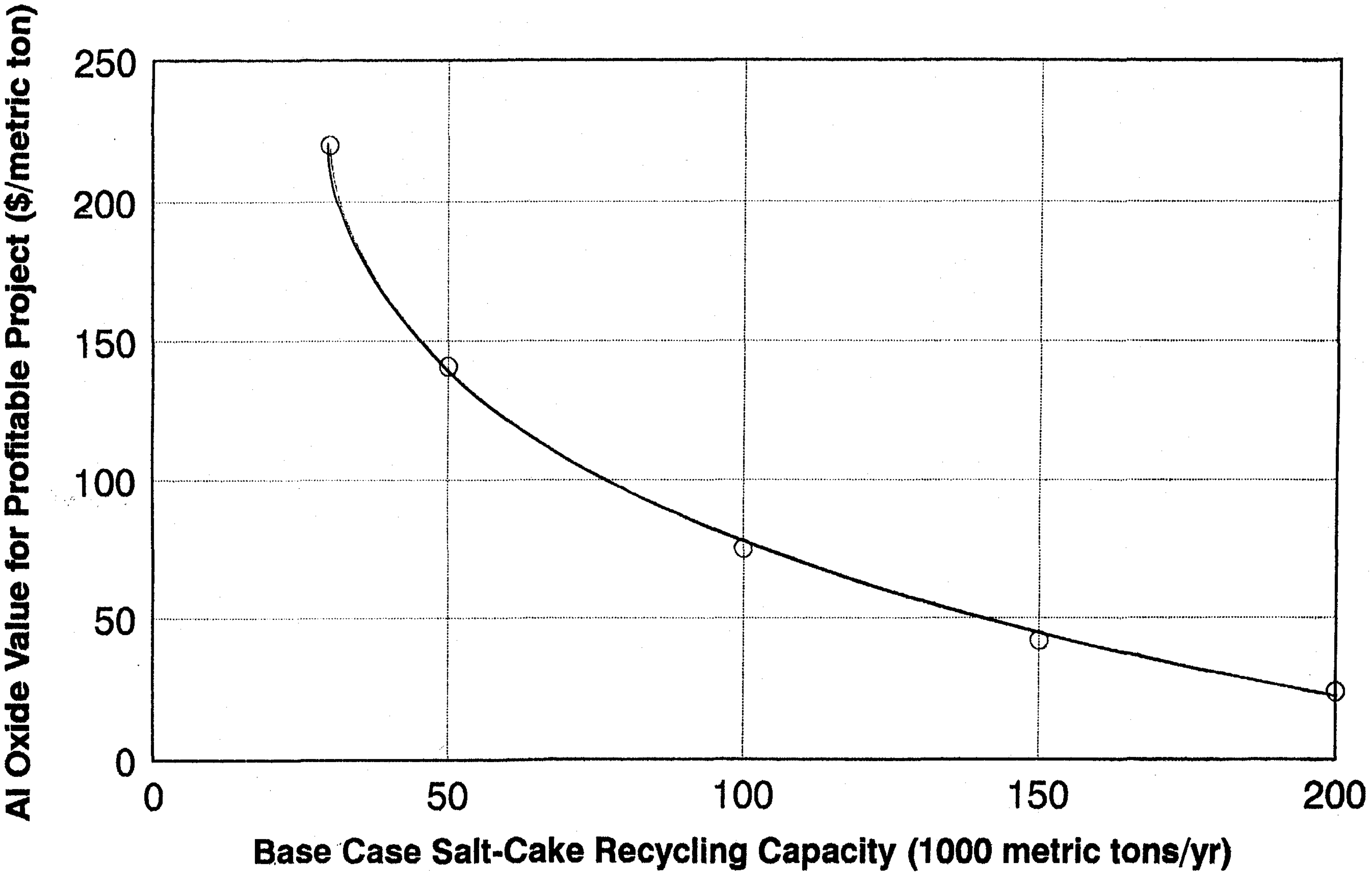


Figure 6: Effect of Capacity on Economics of Salt-Cake Recycling



THE ECONOMICS OF SALT CAKE RECYCLING

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Abstract

The Process Evaluation Section at Argonne National Laboratory (ANL) has a major program aimed at developing cost-effective technologies for salt cake recycling. This paper addresses the economic feasibility of technologies for the recovery of aluminum, salt, and residue-oxide fractions from salt cake. Four processes were assessed for salt recovery from salt cake: (1) *base case:* leaching in water at 25°C, with evaporation to crystallize salts; (2) *high-temperature case:* leaching in water at 250°C, with flash crystallization to precipitate salts; (3) *solvent/antisolvent case:* leaching in water at 25°C, concentrating by evaporation, and reacting with acetone to precipitate salts; and (4) *electrodialysis:* leaching in water at 25°C, with concentration and recovery of salts by electrodialysis. All test cases for salt recovery had a negative present value, given current pricing structure and 20% return on investment. Although manufacturing costs (variable plus fixed) could reasonably be recovered in the sales price of the salt product, capital costs cannot. The economics for the recycling processes are improved, however, if the residue-oxide can be sold instead of landfilled. For example, the base case process would be profitable at a wet oxide value of $220/metric ton. The economics of alternative scenarios were also considered, including aluminum recovery with landfilling of salts and oxides.