RECOVERY OF ELECTROLYTE FROM WASTE ALUMINUM REDUCTION CARBONACEOUS POT LININGS

by

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A THESIS

submitted to

OREGON STATE COLLEGE

in partial fulfillment of
the requirements for the
degree of

MASTER OF SCIENCE

June 1951

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Date thesis is presented April 28, 1951

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ACKNOWLEDGMENT

An expression of indebtedness is due to Dr. William E. Caldwell for his guidance, patience, and understanding during the course of this investigation. The author is also thankful to Dr. Caldwell and Professor Joseph Schulein for permitting him to accompany them on an inspection trip of the Aluminum Company of America aluminum reduction plant at Vancouver, Washington.

The author would also like to express his appreciation and thanks to Dr. J. P. Mehlig for his valuable council and his advice on analytical problems.

Appreciation is expressed to the Aluminum Company of America and the Reynolds Metals Company for samples of the waste aluminum pot liner.

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INTRODUCTION

The foundation of the aluminum industry of the world is the electrolytic process, discovered simultaneously by Hall and Héroult (5,p.88) in 1886, in which aluminum oxide is electrolyzed in a bath of molten cryolite, Na_3AlF_6.

Operation of an aluminum pot

In the modern application of this process, the electrolysis is carried out in a large rectangular iron pot that has a heavy carbonaceous lining which acts as the cathode. This lining is composed of powdered anthracite coal, calcined petroleum coke, and a petroleum pitch binder. Carbonaceous rods, which are lowered into the pot, act as anodes and are made of the same materials.

In starting a pot, the anodes are lowered until they contact the cathode and an arc is struck. A current of fifty thousand amperes at five volts is used. As soon as the arc is struck, powdered cryolite is added and is melted by the heat of the arc.

When a sufficient amount of the molten bath is formed, aluminum oxide is added until the bath is brought up to the proper level, the anodes being raised as the bath level rises. A small amount of fluorspar, CaF_2, is used to lower the melting point of the mixture, and the pot operates at a temperature of 950° to 975°C.

The exact cell reaction is not clearly known but can be represented by the equation,

$$2\ Al_2O_3 = 4\ Al + 3\ O_2$$

The aluminum is discharged at the cathode sides and bottom of the pot and collects in a layer beneath the bath materials. The aluminum is liquid, since the temperature of the pot is above the melting temperature of aluminum, 660°C. Oxygen is liberated at the anodes where it immediately combines with the carbonaceous material to form CO_2.

The manufacture and maintenance of the liner and anodes

The carbonaceous anodes are constantly being lowered, burned away, and replaced. Since an aluminum plant has hundreds of pots, each with twenty-four anodes, the problem of manufacturing these anodes is considerable. The carbonaceous material for the anodes is molded while soft into cubes about fourteen inches on a side and baked in a floor level electric furnace. So many of these anodes are used that the furnaces and molding facilities for their manufacture constitute nearly half of the entire aluminum plant area.

The lining of the pot also is soft when it is first mixed and is tamped into the pot to a thickness of about twelve inches. As the pot is heated the liner quickly hardens.

An aluminum reduction pot liner has an average life of about seven hundred days, by which time the liner has soaked up about two-thirds of its weight in electrolyte.

For instance, sixty pounds of pot liner soaks up forty pounds of electrolyte making one hundred pounds in all. About forty per cent of this is electrolyte. Some of the carbonaceous material has been burned away also, permitting heat to be conducted to the iron pot making the pot red hot. When this occurs, the anodes are raised, the electrolyte and aluminum are siphoned out, and the pot liner is dug out with the aid of a pneumatic hammer. Sometimes holes develop in the liner before it is deemed entirely useless and then the liner is merely patched. The liner plus the seeped-in electrolyte weighs about ten thousand pounds of which about forty per cent, or four thousand pounds, is electrolyte.

Since no satisfactory method for separating the electrolyte from the carbonaceous liner has been perfected, the discarded liner with the absorbed electrolyte is thrown away.

Magnitude of fluorine compound lost to the pot liner

At the Aluminum Company of America's reduction plant at Vancouver, Washington, one complete liner is discarded every day and enough parts of other liners are discarded to make up another ten thousand pounds. Of this twenty thousand pounds of waste pot liner, about forty per cent or eight thousand pounds is electrolyte. Part of it is stock-piled but most of it is thrown over a bank at the edge of the Columbia river.

At the Troutdale plant of the Reynolds Metals Company, 6,750,000 pounds of fluorine compounds are bought per year. Of this, about forty per cent or 2,700,000 pounds is absorbed in the pot liners and thrown away.

The Vancouver plant of the Aluminum Company of America is larger than the above-mentioned Troutdale plant by a ratio of five to four and has to replace about 3,375,000 pounds of absorbed fluorides a year.

This investigation is therefore of industrial importance as an attempt to separate the valuable, and heretofore wasted, electrolyte material from the waste aluminum reduction carbonaceous pot liner.

Consideration of recovery methods for the electrolyte from the waste aluminum pot liner

In any separation or concentration problem in an industrial process two methods of attack are open to the researcher; (a) a procedure depending on the physical properties of the substance in question and (b), a procedure utilizing the chemical properties of the substance.

Processes in the first class use ore dressing machines such as jigs, Wilfley tables, electromagnetic separators, electrostatic separators, air flotation machines, and leaching tanks.

Separation methods utilizing the chemical properties of the substance in question usually form new compounds that are more easily recovered than the original substance.

Air flotation

Since a Federal Laboratory Air Classifying Unit B,(2), was available, it was decided first to try to separate the electrolyte from the pot liner by air float means. This machine has two cyclones in series and gives three size fractions.

Since the specific gravity of carbon as graphite is 2.09 to 2.33 and the specific gravity of cryolite is 3, (2,p.465) it was thought that if the pot liner could be properly classified in a certain size range it would be possible to separate the electrolyte from the carbonaceous material by means of the cyclone.

Microscopic analysis of different size ranges of the pot liner showed that the -200 mesh product was the most nearly separated into particles containing only electrolyte or only carbon and consequently was the product used in the cyclone.

Classification or separation of particles by a moving stream of air depends on two things, the size, and the specific gravity of the particle. Two particles of the same specific gravity but different size can be separated, and two particles of the same size but different specific gravity can be separated.

The cyclone separator is based on the principle of the vortex and operates essentially as follows; dust laden air tangentially enters the top of the cyclone, a cone shaped metal container, and is forced downward in an ever decreasing spiral to the dust outlet trap at the bottom of the cone. Dust particles are precipitated at the periphery of the circularly moving air, the separating effect increasing as the apex of the cone is approached. These particles slide down the sides of the cone in the slower moving air at these points and fall into the dust trap at the apex. This air at the periphery is moving slower because of contact with the cyclone's walls. Clean air, or air containing only certain sized particles depending on how the machine is regulated, forms the vortex in the center and travels upward.

In fewer words it can be said that the cyclone accomplishes particle removal through combined velocity reduction and action of centrifugal forces.

Leaching the pot liner with aluminum salts

Since various methods of leaching are used in many large scale industrial processes, it was decided to try leaching the electrolyte from the pot liner and evaporating the recovered solution to dryness with the idea in mind of feeding the recovered salts back into the electrolytic cell. The one difficulty here, however, was to find a leach solution whose ingredients would not interfere with the operation of the cell.

F. J. Frere (4,pp. 1695-1697) conducted experiments on the solubility of cryolite in aqueous solutions of iron and aluminum salts. A portion of his data is given below. Concentrations are expressed in moles of salt per 1000 moles of water at 25°C.

Reagent	Reagent Conc.	Cryolite Conc.
2 $Al(NO_3)_3$	19.76	14.36
Al_2Cl_6	20.28	11.41
$Al_2(SO_4)_3$	17.04	10.00
2 $Fe(NO_3)_3$	24.88	6.86
2 $FeCl_3$	25.28	1.88
$Fe_2(SO_4)_3$	24.55	3.70

Frere's explanation of the above figures states that, "in the case of the aluminum salts, there is a complete exchange of ions resulting in the formation of aluminum fluoride and the sodium salt of the solvent anion, the aluminum fluoride in turn combining with the aluminum salt present to form a double salt." For example, Na_3AlF_6 reacts with the $AlCl_3$ to form AlF_3 and NaCl. The AlF_3 in turn combines with the $AlCl_3$ of the solvent to form a double salt of $AlCl_3 \cdot AlF_3$.

The above figures indicate that there is a possibility of leaching the electrolyte from the pot lining with salts such as aluminum nitrate. Experimentation is required to verify the quantity of electrolyte recovered in this manner.

Leaching the pot liner with water

When the lining is removed from the pot its color is black, but after being exposed to the weather on a waste dump for a short time a white crust forms on its surface. This is due to hydrolysis, by the moisture of the atmosphere, of the crystals of electrolyte and their subsequent exfoliation to give a fresh and larger surface.

This observation gave rise to the thought that a process involving a plain water leach of the pot liner might, while probably not recovering all of the electrolyte, be economically sound.

Although cryolite itself is only very slightly soluble in water, it was thought that the electrolyte, as it comes from the pot lining might be considerably water soluble.

Volatilization of hydrofluoric acid by treating the pot liner with sulfuric acid

Since volatile acids can be evolved by treating their salts with a less volatile acid, it is possible that a process involving the treatment of the pot liner with concentrated sulfuric acid would be economically feasible. This could be done in a corrosion resistant retort-type furnace with the evolved hydrofluoric acid being caught in a soda or lime water solution. The residue could be extracted to recover a sodium alum.

METHODS OF ANALYSES

Preparation of samples

Although waste pot liner samples were obtained from both the Reynold's Metals Company and the Aluminum Company of America, only the carbonaceous material from the latter company was used in this investigation.

About two hundred pounds of the liner was picked at random, while still hot, from a thirty foot square area of the dump on the bank of the Columbia river. All sizes from powder to chunks eight inches in diameter were selected. This two hundred pounds was coned and quartered by approved methods (1,pp.54-56) until fifty pounds remained. The large chunks of liner were broken with a sledge hammer and the whole sample reduced to two-mesh size in a jaw crusher. This product was comminuted in a pair of six inch rolls until the whole would pass through a ten-mesh screen. Pulverizing with a disk pulverizer was found to be impossible because of the many small pieces of aluminum metal in the sample; also the graphite tended to smear and roll up on the pulverizer plates causing the machine to stall.

When crushing and pulverizing the pot liner, a large amount of dust was formed which was extremely irritating to the eyes and the linings of the nose and throat. In any recovery process involving the crushing and pulverizing of a liner, a closed system would be imperative.

After being coned and quartered, crushed, and run through the rolls five times, no more mixing was considered necessary before screening.

Using Tyler Standard Screens and a Rotap screen shaking machine, the pot liner was then separated into the following size ranges; +28, -35 + 50, -50 + 100, -100 + 150, -150 + 200, and -200 mesh.

Before the samples were analyzed they were dried overnight at 105°C.

Determination of soluble fluorides, carbon, and insoluble materials

In determining the amount of electrolyte present in a sample, the Reynolds Metal Company method of analysis of pot liners was used (6). This method is as follows.

"A one gram sample of finely divided material is weighed into a wide mouth 250-ml. Erlemeyer flask; to this is then added 25 ml. of 30% aluminum chloride solution and 25 ml. of water. The flask is then put on to boil for exactly ten minutes. This procedure renders the fluoride bath materials soluble. The contents of the Erlenmeyer are then filtered through a previously ignited and tared gooch crucible with asbestos matting. The collected precipitate plus gooch crucible are then placed in a drying oven (105^{o}-110^{o}) until they reach a constant weight. This weight subtracted from the one original gram is the bath material present.

"The next step involves ashing the coke remaining in the gooch crucible in a furnace at 950^{o}C. This ashing is continued until a constant weight is arrived at. This loss is then the actual carbon content. The weight left in the gooch crucible is alumina plus ash materials of the original carbonaceous lining."

Unless the ten minute boiling period is rigidly observed erroneous results will be obtained for the per cent of soluble fluorides. In running six samples at a time the leach solutions could not be added at the same time, the solutions could not be brought to the boiling point simultaneously, and in filtering through the gooch crucibles a lapse of about forty-five seconds occurred between the first and last pourings. Consequently, a precision of one per cent in agreement of results was considered good.

Determination of fluorine

The method of analysis for fluorine was one adapted by A. H. MacMillan of the United States Bureau of Mines Northwest Electrodevelopment Laboratory at Albany, Oregon from methods for fluorine by Rowley and Churchill (7,pp.551-552) and Willard and Winter (8,pp.7-10).

This procedure, although originally adapted to the determination of fluorine in phosphate rock, was used very successfully on the liner.

"To a 0.5 gram sample in Claissen flask, add a little water and set up for steam distillation with the bulb of a thermometer immersed in the liquid. The end of the condenser is immersed in about 10 ml. of 20% NaOH.

"Add 10 ml. of perchloric acid to the sample and heat to 120°C., start the steam distillation and hold the temperature between 120°C. and 150°C.; if there is much organic matter present, do not let the temperature rise above 135°C. Distill over 100 ml. It is best to replace the receiving beaker with a new one and distill over a second 100 ml. portion to be sure that all the fluorine is distilled. Do not add any silica powder to the sample to furnish silica as it becomes gelatinous and holds fluorine. Use about three glass beads to furnish silica and protect the flask.

"After distillation if there is more than 50 mg. of fluorine present in the distillate, take an aliquot so that the fluorine is between 1 and 50 mg. Dilute the distillate to 100 ml. and add 8 drops of alizarin indicator, neutralize with 1-1 HCl and then adjust the acidity of the solution back and forth with two per cent NaOH and 1-200 HCl, leaving the solution with the pink color just discharged. Add one ml. of buffer solution and titrate with 0.1 N thorium nitrate to a pink color."

The theory of the procedure is that the perchloric acid reacts with the fluorides to form fluosilicic acid which is steam distilled into the NaOH. Sodium fluosilicate is formed and reacts with the thorium nitrate when titrated to form a precipitate of thorium fluoride.

At the end point of the titration the precipitate of white thorium fluoride becomes colored pink from the adsorption of the indicator on the precipitate. This pink color is more easily seen if the precipitate is allowed to settle, although this is not necessary after getting used to the titration.

A blank determination should be made. Standardize the thorium nitrate against a standard fluorine solution made from recrystallized lithium fluoride or sodium fluosilicate.

Reagents:

Sodium alizarin sulfonate, 0.05 g. in 100 ml. water

Buffer solution, 2.000 g. NaOH in 100 ml. of water to which is added 9.448 g. of monochloracetic acid

0.1 N thorium nitrate, 13.8055 g. per liter

In this investigation, instead of standardizing the thorium nitrate with lithium fluoride or sodium fluosilicate, United States Bureau of Standards Phosphate Rock samples 56B (3.4%F), and 120 (3.76%F) were treated in the reaction flask in the same way as were the samples to be determined. They were reacted and steam distilled, and the resulting solution titrated with the thorium nitrate solution. In standardizing the thorium nitrate with one standard sample, it was possible to check the other within ± 0.02%.

Determination of Aluminum

Extreme difficulty was experienced in finding a rapid and accurate method for the determination of aluminum in the pot liner. Commercial methods for the analysis of aluminum in ores and alloys, although accounting for all interfering elements and radicals, require about two days for completion. Since time was critical it was considered desirable to develop a method suited to the analysis of the pot liner alone.

A quarter-gram sample was fused in a nickel crucible with sodium peroxide. The fusion was poured on a copper plate, then taken up with HCl in a casserole. H_2SO_4 was added and the solution taken to H_2SO_4 fumes and then to a red heat to destroy fluorides which hinder the precipitation of aluminum as the hydroxide. The residue was taken up with water and HNO_3 and after adding NH_4Cl to prevent precipitation of magnesium, the $Al(OH)_3$ was precipitated by use of ammonium hydroxide. Theoretically, nickel does not interfere in this precipitation but in this case with a large excess of nickel from the fusion in the nickel crucible, the hydroxide was deeply colored with the occluded nickel ammonia complex. This precipitate was then dissolved in HNO_3 and the solution made basic with NaOH to tie up the aluminum as the soluble sodium aluminate and precipitate the nickel as the green $Ni(OH)_2$. This hydroxide of nickel has the peculiar property of being very slimy and it is extremely difficult to wash completely clean. The solution was then boiled and potassium persulfate ($K_2S_2O_8$) was added to oxidize the nickel to the plus four state. The plus four nickel, which precipitated as the black

$Ni(OH)_4$, was then filtered off. This plus four nickel hydroxide was somewhat similar to aluminum hydroxide in that it occluded no ions and was comparatively easy to wash clean. The aluminum in the filtrate was then reprecipitated as the hydroxide, giving a clean white precipitate that was ignited and weighed as Al_2O_3.

Determination of sodium

The method for the determination of sodium in the original pot liner and in the solution obtained from the water leach of the pot liner is as follows.

The original liner was refluxed twelve hours with concentrated sulfuric acid to partially oxidize the carbon and free all the sodium containing compounds, and to convert the sodium in these compounds to the soluble sulfate. The remaining carbon was then filtered off. From this point the analysis of the liner and the leach water was the same. Aluminum was separated by the method given previously. A test for calcium here in the procedure revealed only a trace. The solution was then fumed to dryness with sulfuric acid in a weighed platinum dish. Powdered ammonium carbonate was added to the residue which was heated until no more fumes appeared. This last treatment was to remove any remaining sulfuric acid. Finally the dish was reweighed, the difference being taken as sodium sulfate.

EXPERIMENTAL RESULTS

Summary of analyses of the original pot liner

Analysis of the pot liner with methods previously described gave for it the following average composition.

Carbon	41.6%
Aluminum	16.4%
Fluorine	15.3%
Sodium	19.0%

The remainder was oxygen from some Al_2O_3 that had also seeped into the liner, a small amount of calcium from the CaF_2 that was added to the electrolyte, and a slight amount of insoluble material from the original constituents of the liner itself.

Aluminum chloride leach results

Using the Reynolds Metal Company methods for determining soluble fluorides with an aluminum chloride leach; it was found that with one-gram samples, results below were obtained.

Sample No.	Weight	Size	% C	%Soluble	% Insol.
1	1g	-80+100	47.0	44.7	8.3
2	1g	-100+150	44.8	46.5	8.7
3	1g	-200	41.6	49.6	8.7

This indicated that the particles of the larger sized fractions were not completely broken down into only electrolyte and only carbon, some of the electrolyte probably being enclosed by the carbon.

Aluminum nitrate leach results

Since in any commercial adaptation of the leach to recover the electrolyte the chloride might be deleterious to the electrolysis reaction in the aluminum pot, an aluminum nitrate leach was tried. The nitrate would be more easily destroyed than the chloride. To destroy the nitrate salts, a process employing heat could be used, the products being aluminum oxide and nitrogen oxides. These nitrogen oxides, in turn, could be collected and used for making nitric acid and in turn more aluminum nitrate. A 30% aluminum nitrate solution and the same procedure was used as in the aluminum chloride leach. Results are as follows.

Wt. Sample	Mesh	% Soluble
1g	-200	41.6
2g	-200	40.2
3g	-200	30.0
1g	-100+150	33.0
2g	-100+150	30.8

Obviously the $Al(NO_3)_3$ does not perform as well as the $AlCl_3$. Best results were obtained with the finer size particles and the smaller sample weights.

Water leach results

The first indication that a leach method might be the solution to the problem at hand was given by the observation that the black freshly crushed pot liner became flecked with white after being exposed to the air for some time. This was apparently due to the absorption by the electrolyte of moisture from the atmosphere which caused a swelling up or exfoliation of the crystals of the electrolyte.

This seemed to indicate that a water leach of the material might extract enough of the material to make the process economically sound. Extracting and saving even fifty per cent or less of the electrolyte would be better than throwing it away.

Consequently samples of varying weighs were leached, first with 50 ml. of water. The -200 mesh material was used, and was boiled exactly ten minutes. Varing weights of samples were used in order to determine the unit amount of water that would recover the maximum amount of electrolyte. Results are as follows:

Sample No.	Weight	% Soluble
1	1g	26.2
2	1g	26.4
3	2g	22.8
4	2g	23.1
5	3g	22.1
6	3g	21.7

The leached solution had a pH of about 11 as given by universal indicator paper.

With the one-gram sample, fifty grams of water were used to extract 0.26 grams of electrolyte.

One, two, and three-gram samples of the -200 mesh material were also leached with both forty and thirty milliliters of water in order to determine the unit amount of electrolyte that was dissolved by the minimum amount of water. Results are shown below.

40 ml. leach

Sample No.	Weight	% Soluble
1	1g	26.6
2	1g	25.6
3	2g	22.7
4	2g	22.7
5	3g	21.4
6	3g	21.5

30 ml. leach

Sample No.	Weight	% Soluble
1	1g	23.1
2	1g	23.6
3	2g	21.8
4	2g	21.9
5	3g	20.8
6	3g	21.0

The above figures are demonstrated more clearly by the graph on the next page.

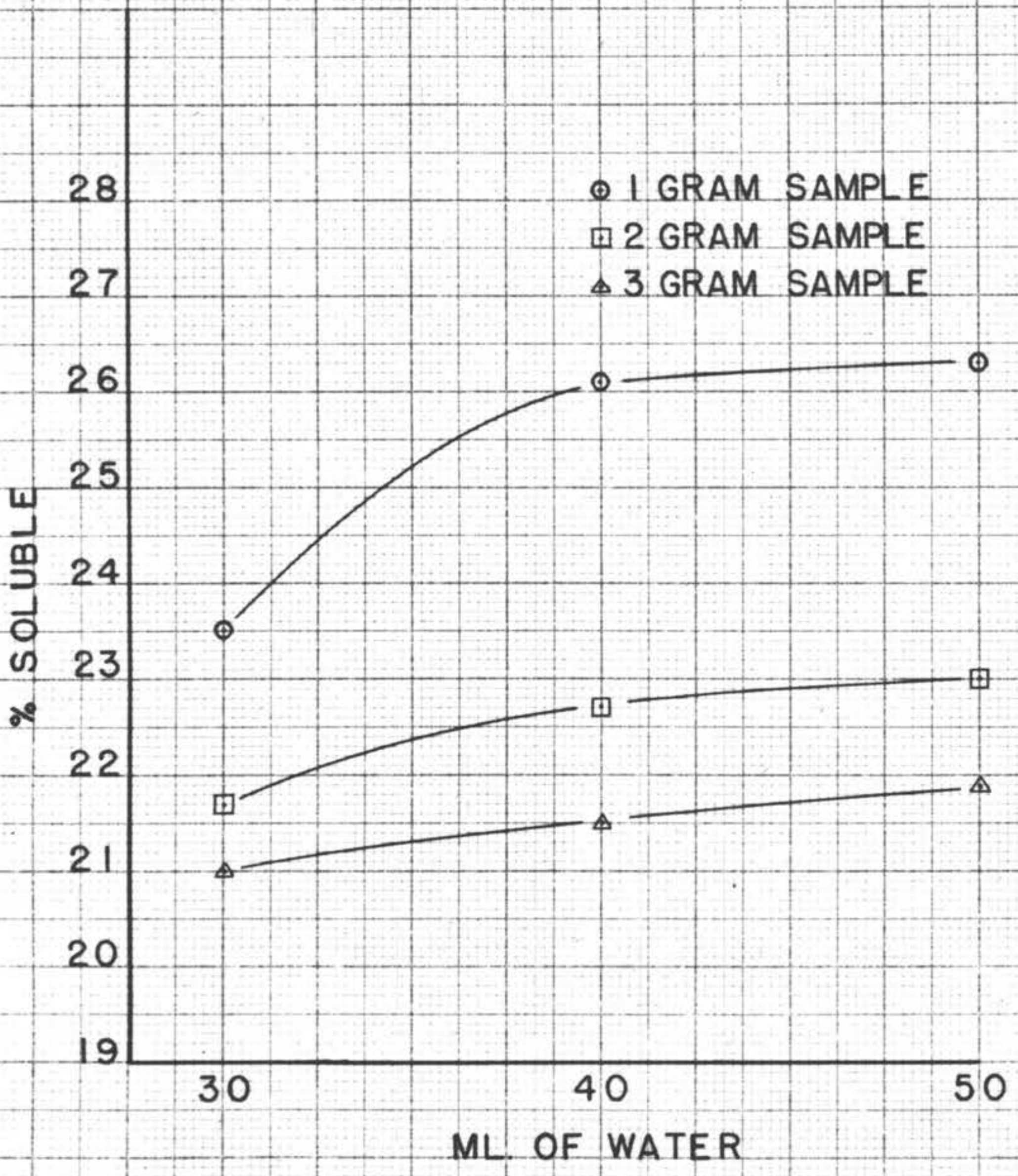
To determine just how much of each element in the pot lining was leached out by the water, both the recovered solutions after the leach and the residues from the leach were analyzed for fluorine and aluminum. The leached solution was also analyzed for sodium.

Sample	Wt.	% Na Leached Out	% Al Leached Out	% Al in residue (by difference)	% F Leached Out	% F in resid.
1	1g	12.1	2.0	14.4	7.96	7.88
2	1g	12.1	2.0	14.4	7.63	8.07

The fluorine from the leach and the leached residue of the first sample totaled 15.8% while the total for the second leach solution and residue was 15.7%.

In other words, approximately half of the actual fluorine content of the pot liner was removed by a water leach and approximately one-third of the electrolyte removed in the water leach was actually fluorine. Verification of the analysis for fluorine in the original pot liner is to be noted by the adding of the amount of the fluorine of the leach and the fluorine of the leached residue. The sum of these two values is almost exactly the same as the per cent of fluorine in the original liner.

RELATIONSHIP OF % SOLUBILITY OF ELECTROLYTE TO AMOUNT OF WATER USED IN LEACH



Air flotation analyses

One pass through the air float separator will give three size fractions; coarse, medium, and fine. The course and medium fractions are collected at the base of each cyclone and the fines are deposited in the tailing bags. It was not practical to analyze the tailing after each run because the bags were not easily cleaned and would have to be replaced new each time a run was made. Very little of the material that was run through the machine passed into the bags.

With the V valve set at 18, five runs were made with the M valve set at 10, 11, 12, 13, and 14. Five runs were made at the above M valve settings for V valve settings of 20 and 22 also. With two samples collected for each run thirty samples were collected in all. These were assayed by the aluminum chloride leach method for soluble fluorides giving the following results.

Sample No.	V Setting	M Setting	Course Fraction %fluorides	Medium Fraction %fluorides
1	18	10	46.8	45.8
2	18	11	46.2	46.6
3	18	12	46.7	47.2
4	18	13	46.6	46.1
5	18	14	47.2	46.5
6	20	10	46.2	45.3
7	20	11	46.1	45.8
8	20	12	45.6	46.4

Sample No.	V Setting	M Setting	Course Fraction %fluorides	Medium Fraction %fluorides
9	20	13	45.4	46.6
10	20	14	46.0	45.8
11	22	10	46.1	46.2
12	22	11	46.1	45.5
13	22	12	46.6	46.3
14	22	13	46.8	45.4
15	22	14	47.2	46.5

Complete tabulations of data for the experimental results given in this section are to be found in the appendix, page 32.

DISCUSSION OF RESULTS

The purpose of this investigation has been the determination of the factors involved in recovering absorbed electrolyte from waste aluminum carbonaceous pot linings.

A summary of averages of the analyses of the pot lining is as follows.

Aluminum	16.4%
Fluorine	15.3%
Carbon	41.6%
Sodium	19.0%

An average of 46.9% of the total weight of the pot liner was soluble in a fifteen per cent aluminum chloride leach solution and 41.6% was soluble in a fifteen per cent aluminum nitrate leach solution. The aluminum chloride in the recovered salts would be detrimental to the cell operation if the salts were re-fed to the cell. The aluminum nitrate could be easily converted to the oxide and the nitrogen oxides recovered.

Twenty-six per cent of the pot lining was soluble in boiling water. The aluminum, fluorine, and sodium content of this water soluble part represented respectively 2.0%, 7.8%, and 12.1% of the total weight of the lining. These figures show that one-eighth of the aluminum, about one-half of the fluorine, and sixty per cent of the sodium in the original sample is water soluble.

In any further study of the application of the leach method to an industrial process for the recovery of the electrolyte from the pot lining, a determination of the minimum amount of water or leach solution per unit amount of electrolyte dissolved would have to be made.

Almost exactly the same per cent fluorine in the original liner was obtained by using sulfuric acid as was by using perchloric acid in the analysis for fluorine. This observation gives rise to the thought of the possible commercial treatment of the waste aluminum pot lining with concentrated sulfuric acid to evolve and recover hydrofluoric acid. The gas could be bubbled through a soda or lime water solution to make a salt suitable for re-feeding to the electrolytic cells.

Little , if any, separation of the electrolyte from the carbonaceous material of the liner was obtained by air flotation. This attempt to utilize air flotation was based on the differing specific gravities of the carbonaceous material and the electrolyte. Perhaps better results would have been obtained if all the particles that were run through the cyclone at one time were of exactly the same size. Obviously, accurately sizing the particles would not be economically possible in an industrial process.

SUMMARY

1. A water leach of the pulverized aluminum reduction carbonaceous pot lining recovers up to fifty-two per cent of the electrolyte that is absorbed by the lining. This method could be used alone or in conjunction with some method such as foam flotation for the recovery of the heretofore-wasted electrolyte.

2. An aluminum nitrate leach of the pot lining recovers eighty-five per cent of the electrolyte from the carbonaceous material. The salts, recovered by evaporating the leach solution, could be re-used in the electrolytic cell if they were first heated to convert the aluminum nitrate to the oxide.

3. A sulfuric acid treatment of the pot lining evolves an amount of hydrofluoric acid from the fluoride salts equal to that evolved by perchloric acid. The hydrofluoric acid could be utilized to convert lime, soda, and aluminum to their fluoride salts which could be re-fed to the electrolytic cell.

4. Air flotation methods do not separate the electrolyte from the carbonaceous material.

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APPENDIX

$AlCl_3$ leach -200 mesh

No.	wt.	wt.C + insol.	wt. C	% sol.
1	1g	0.5310g	0.4440g	46.9
2	1g	0.5307g	0.4410g	46.9
3	1g	0.5307g	0.4410g	47.0

$Al(NO_3)_3$ leach -200 mesh

No.	wt.	wt.C + insol.	wt. C	% sol.
1	1g	0.5814g	0.4380g	41.9
2	1g	0.5859g	0.4430g	41.4
3	1g	0.5831g	0.4483g	41.7
4	2g	1.1748g	0.8921g	41.3
5	2g	1.1976g	0.8901g	40.2
6	2g	1.2068g	0.8889g	39.7
7	3g	1.9812g	1.3230g	----
8	3g	2.1230g	1.3290g	29.2
9	3g	2.0576g	1.3183g	31.4

$Al(NO_3)_3$ leach +100 + 150 mesh

No.	wt.	wt. C + insol	% sol.
1	1g	0.6800g	32.0
2	1g	0.6694g	33.1
3	1g	0.6564g	34.4
4	2g	1.3839g	30.3
5	2g	1.3850g	30.8
6	2g	1.3664g	31.7

Standardization of $Th(NO_3)_4$

No.	Sample	wt.	$Th(NO_3)_4$ Bur.	Stds. assay % F	Calc.% F
1	B.S.120	1g	20.02 ml.	3.76	----
2	B.S.120	1g	20.05 ml.	3.76	----
3	B.S.56B	1g	18.57 ml.	3.40	3.38
4	B.S.56B	1g	18.55 ml.	3.40	3.38

Results 3-4 1 ml T h$(NO)_4$ 0.001876 g fluorine

Determination of Fluorine in water leach of -200 mesh pot lining.

No.	Wt.	% sol.	made up to	Aliquot	$Th(NO)_4$	% F
1a	1g	26.6	250ml.	50ml.	7.60ml.	7.93
1b	1g	26.6	250ml.	50ml.	7.65ml.	7.99
2	1g	26.1	250ml.	50ml.	7.50ml.	7.80

Determination of Fluorine in residues from above leaches

No.	Wt.residue	made up to	aliquot	$Th(NO_3)_4$	% F
1	0.7336g	12.62ml.	150ml.	12.62ml.	7.88
2	0.7388g	17.20ml.	200ml.	17.00ml.	8.07

Fluorine analysis on original pot liner using $HClO_4$

No.	wt.	made up to	aliquot	$Th(NO_3)_4$	% F
1	1g	500 ml.	100 ml.	16.2 ml.	15.2
2	1g	500 ml.	100 ml.	16.3 ml.	15.3

Fluorine determinations on original pot liner using H_2SO_4

No.	wt.	made up to	aliquot	$Th(NO_3)_4$	% F
1	1g	500 ml.	100 ml.	10.50 ml.	15.5
2	1g	500 ml.	100 ml.	10.50 ml.	15.5

Sodium and Aluminum determinations on original liner

No.	wt.	wt. Na	% Na	Wt. Al	% Al
1	0.25g	0.0475	19.0	0.0415g	16.6
2	0.25g	0.0477	19.0	0.0406g	16.2
3	0.25g	0.0480	19.4	0.0404g	16.1

Sodium and Aluminum determinations on water leach of liner

No.	Wt.	% sol.	Wt. Na	% Na	Wt. Al	% Al
1	1g	26.8g	0.1174	11.7	0.0201g	2.0
2	1g	26.3g	0.1133	11.3	0.0202g	2.0
3	1g	26.2g	0.1140	11.4	0.0205g	2.0