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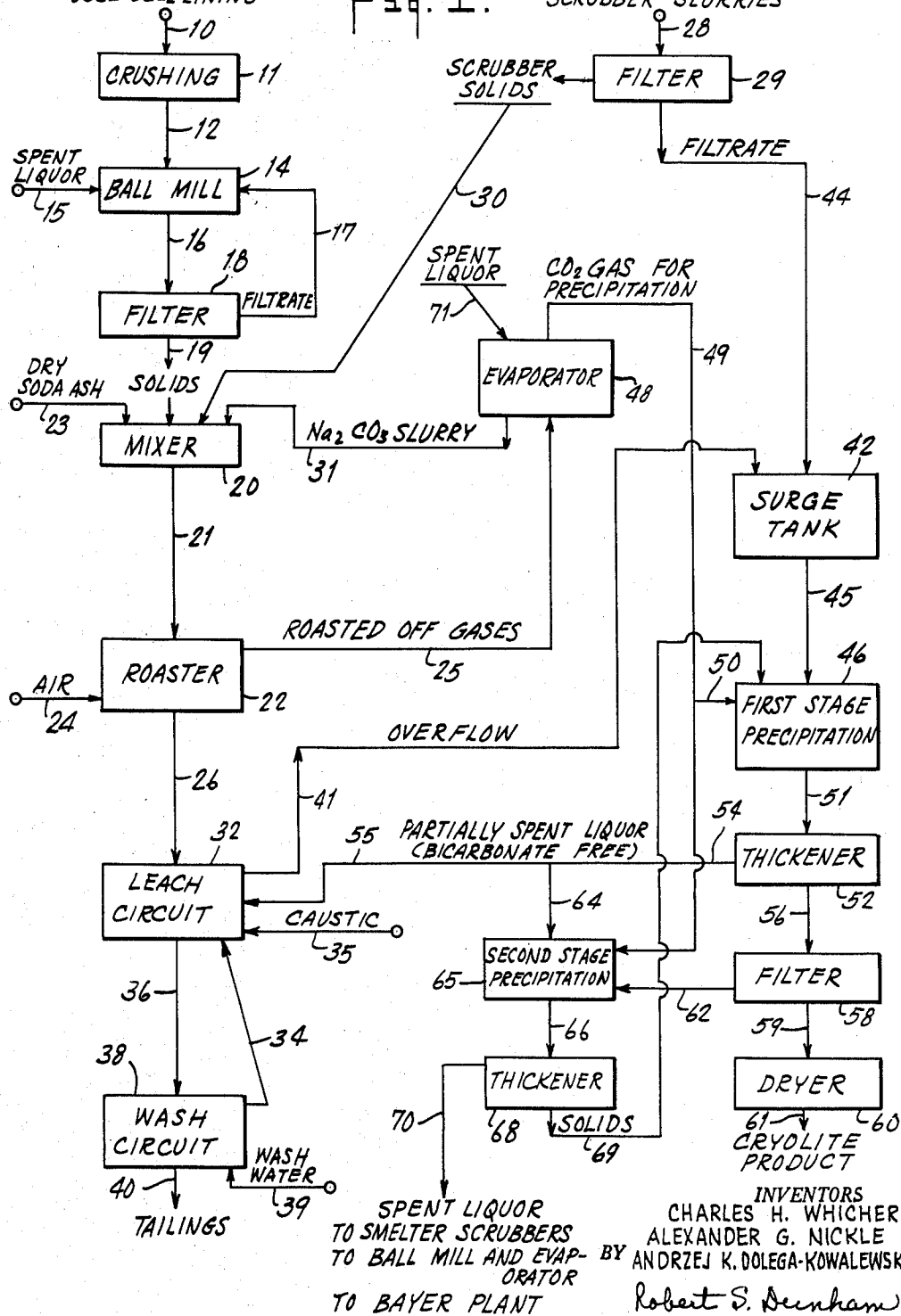
RECOVERY OF CRYOLITE

2 Sheets-Sheet 1

USED CELL LINING

Fig. 1.

SCRUBBER SLURRIES



Oct. 8, 1963

C. H. WHICHER ETAL

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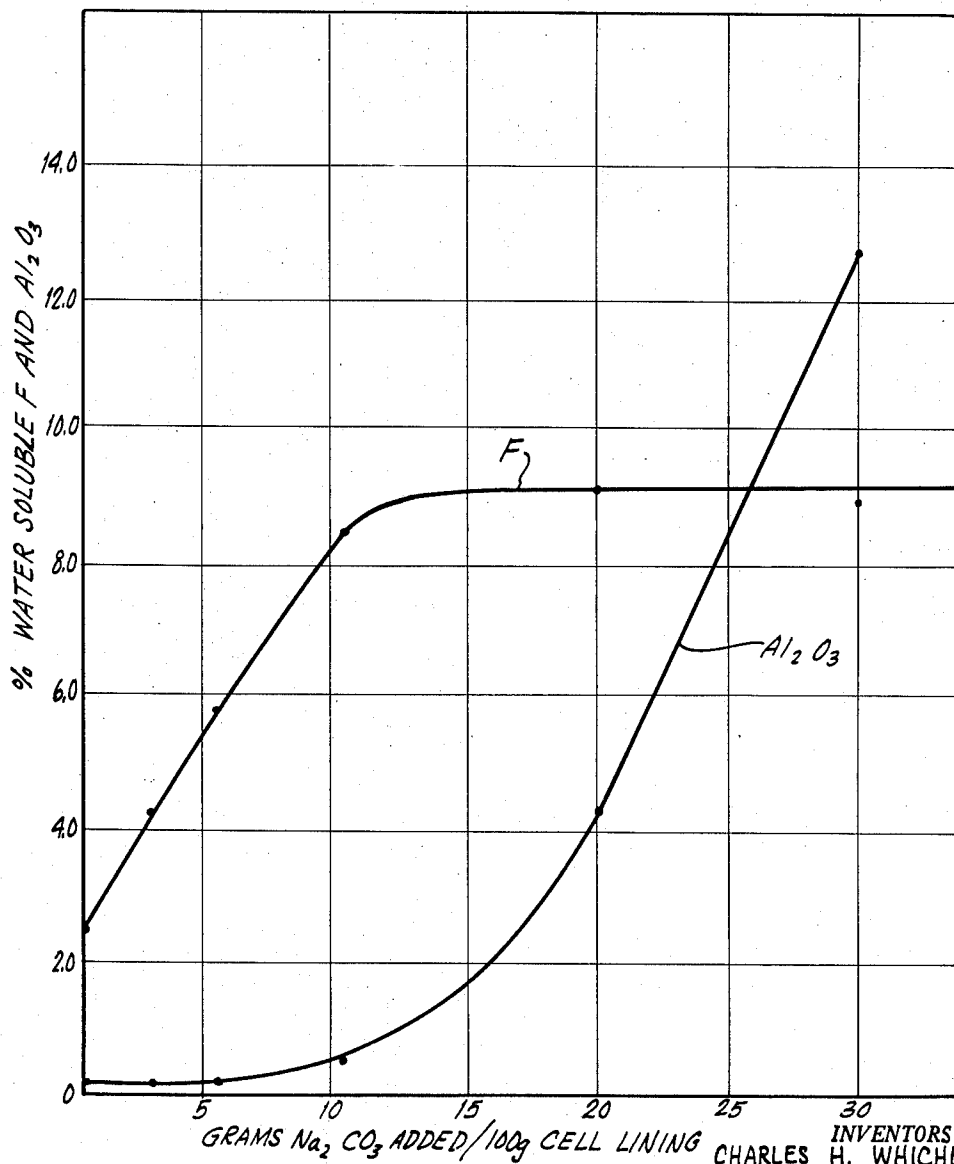
RECOVERY OF CRYOLITE

Filed April 3, 1961

2 Sheets-Sheet 2

Fig. 2.

THE EFFECT OF INCREASING SODA ON THE SOLUBILITY OF
FLUORIDE AND Al_2O_3 IN USED CELL LINING AFTER ROASTING



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RECOVERY OF CRYOLITE

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9 Claims. (Cl. 23—88)

This invention relates to the recovery of cryolite from the lining of electrolytic cells used for the production of aluminum wherein an electric current is passed through a molten bath of cryolite (Na_3AlF_6) containing alumina (Al_2O_3) dissolved therein.

The electrolytic cell is made up of a sturdy steel outer shell and an inner lining of a heavy impervious layer of baked electrically conductive carbon which forms the cathode of the cell; to control heat losses the cell is usually insulated by a layer of insulating powder or brick placed between the carbon lining and the external steel shell. Eventually, however, the carbon lining of the cell deteriorates with use due to the penetration of the electrolytic bath and products of electrolysis resulting ultimately in warping and even the formation of fissures and cracks at which time the cell must be taken out of service and the lining replaced.

It has been found to be economical to recover any cryolite in the carbon cell lining particularly when it contains a substantial amount of cryolite admixed therein, such as an amount of cryolite in the range of 10% to 30% by weight more or less.

Various methods and techniques have been suggested and employed for the recovery of cryolite values or the admixture of sodium fluoride (NaF) and aluminum fluoride (AlF_3) from the used carbonaceous lining. For instance, it has been proposed to recover fluoride values such as cryolite from the used carbonaceous cell lining material by treating finely divided cell material with an aqueous caustic solution to effect reaction between the fluoride values or cryolite therein with sodium hydroxide (NaOH) to yield water soluble sodium fluoride and water soluble sodium aluminate (NaAlO_2) and then to treat the resulting solution to precipitate cryolite therefrom. This method of recovering cryolite from cell lining material suffers from the disadvantage of requiring a considerable amount of excess sodium hydroxide which is costly while the time necessary to effect the reaction is somewhat prolonged with the further disadvantage that it is accompanied by much foaming due to gas formation and lastly the product is contaminated with alumina.

Accordingly, it is an object of this invention to provide an improved process for the recovery of fluoride values, such as cryolite, from materials containing the same.

It is another object of this invention to provide an improved process for the recovery of cryolite from used carbonaceous cell lining material containing cryolite admixed therewith.

Still another object of this invention is to provide a process for the recovery of cryolite from carbonaceous cell lining material containing cryolite admixed therewith wherein improved yields of recovered cryolite are obtainable.

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How these and other objects of this invention are achieved will become apparent in the light of the accompanying disclosure made with reference to the accompanying drawings wherein:

FIG. 1 is a flow diagram or flow chart illustrating various steps in the process of this invention; and

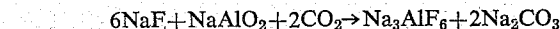
FIG. 2 graphically illustrates the influence of a reactant, sodium carbonate, employed in the process of this invention upon the solubility of fluoride-containing material and alumina in the cell lining material when treated in accordance with the practice of this invention.

In accordance with this invention we have provided an improved method for the recovery of fluoride or fluorine values, such as cryolite, from material containing the same, such as used carbonaceous cell lining material employed in the electrolytic reduction or refining of aluminum, by contacting said material at an elevated temperature with an amount of a water-soluble metal carbonate, such as sodium carbonate, sodium bicarbonate or an admixture thereof, under conditions, particularly of time and temperature, to effect reaction between cryolite and the added carbonate in accordance with the following chemical equation:



In the accompanying disclosure carbonate is meant to include carbonate, bicarbonate and carbonate and bicarbonate-containing mixtures.

As a result of the foregoing reaction, fluoride material, such as cryolite, is converted to water-soluble materials, such as sodium fluoride and sodium aluminate. Following the above-described conversion operation, the resulting reaction admixture containing sodium fluoride and sodium aluminate is contacted with an aqueous solution to extract or dissolve the water soluble sodium fluoride and sodium aluminate therefrom. The resulting aqueous solution, now containing sodium fluoride and sodium aluminate dissolved therein, is then contacted with carbon dioxide (CO_2) to precipitate cryolite therefrom in accordance with the following chemical equation:



The precipitated cryolite is then separately recovered and may then be re-used in the electrolytic cell.

The reaction between cryolite and the water-soluble carbonate, such as sodium carbonate, to yield water-soluble sodium fluoride and sodium aluminate is carried out at an elevated temperature, such as a temperature of about 500°C . or lower. Faster reaction rates are possible at higher temperatures; a satisfactory reaction rate is attainable at a temperature of about 800°C . or even higher, such as a temperature of about 900°C . more or less. At about 900°C ., however, the cell lining material being treated tends to become sticky and more difficult to handle. Accordingly, it is preferred to carry out the roasting or high temperature conversion operation at a temperature not greater than about 875°C ., however, if there is not enough soda present to react with all the cryolite the mixture will get sticky at a temperature lower than normal and, furthermore, the presence of soda permits much faster heating rates.

During the high temperature roasting operation substantially all the cryolite contained in the cell lining material is converted to sodium fluoride and sodium aluminate.

These materials can then be readily leached out of the remaining solid gangue materials by water, preferably hot water, or by a dilute caustic solution, such as an aqueous caustic solution containing less than about 1% by weight sodium hydroxide, e.g. an amount of sodium hydroxide of about 2 grams per liter. The resulting aqueous solution is then treated by contact with carbon dioxide, preferably gaseous carbon dioxide, to precipitate cryolite therefrom together with the formation of sodium carbonate which remains dissolved in the aqueous solution. The resulting aqueous solution or spent liquor can then be treated for the recovery of sodium carbonate therefrom or employed directly to treat additional cell lining material for the recovery of cryolite therefrom.

Reference is now made to the drawings, particularly FIG. 1 which illustrates by way of a flow chart, an embodiment of this invention directed to the recovery of cryolite from used carbonaceous cryolite-containing cell lining material and from the solids which result from cleaning the gases escaping from the electrolytic cells. The used carbonaceous cell lining material to be treated in accordance with this invention may have the chemical analysis set forth in the accompanying Table I.

TABLE I

Chemical component:	Percent by weight
Cryolite	16.6
Sodium fluoride	11.0
Sodium hydroxide	3.0
Sodium carbonate	7.0
Caustic soluble alumina ¹	11.0
Inert alumina	26.6
Carbon or similar carbonaceous material	20.0
Calcium fluoride	3.3
Other materials (by difference)	1.5

¹ Caustic soluble aluminum compounds expressed as Al_2O_3 and corrected for aluminum in cryolite.

The used cell lining material is supplied from a suitable source, not shown, by means of suitable solids handling equipment, not shown, via line 10 to a crushing operation or crusher 11 wherein relatively large size or relatively massive pieces of the cell lining material are reduced to a smaller, more conveniently handled size. From crushing operation 11 the resulting crushed cell lining material is supplied via line 12 to suitable fine grinding equipment such as ball mill 14 wherein the already crushed cell lining material is reduced to a relatively fine size, such as a size below about minus 8 mesh. It is preferred, however, to carry out the grinding operation within ball mill 14 such that the resulting reduced cell lining material has a mesh size below about minus 35 mesh. The smaller the size of the finely reduced cell lining material, the faster the cell lining material (i.e., cryolite therein) reacts with the sodium carbonate in the subsequent roasting or high temperature conversion operation in accordance with this invention.

Desirably, the fine grinding of the cell lining material in ball mill 14 is carried out in the presence of aqueous sodium carbonate-containing solution, such as aqueous sodium carbonate-containing spent liquor, supplied from a suitable source, not shown, via line 15. By carrying out the fine grinding operation in the presence of an aqueous sodium carbonate-containing solution the finely reduced cell lining particles are wetted with a film of aqueous sodium carbonate-containing solution which, upon drying, leaves a residue of sodium carbonate on these particles. This coating or residue of sodium carbonate on the finely-divided cell lining particles serves to supply at least part of the process sodium carbonate requirements in the subsequent high temperature conversion or roasting operation.

Following the fine grinding operation within ball mill 14 the resulting reduced cell lining material is supplied via line 16 to filter 18 which may be a plate and frame filter or a continuous rotary vacuum filter. The aqueous

sodium carbonate-containing filtrate recovered from filter 18 is recycled via line 17 to contact and to wet additional cell lining material undergoing size reduction in ball mill 14.

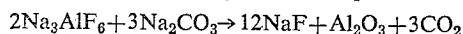
The filtered finely divided solids are removed from filter 18 and supplied via line 19 to solids mixer 20 wherein these solids are mixed with a water soluble carbonate, such as a water soluble alkali metal carbonate, e.g. sodium carbonate or sodium bicarbonate or mixtures thereof. Sodium carbonate is preferred in the practice of this invention, desirably dry, anhydrous sodium carbonate, which is supplied to mixer 20 from a suitable source, not shown, via line 23. It is mentioned, however, that instead of dry sodium carbonate, an aqueous slurry or a concentrated solution of sodium carbonate can be employed to supply all or a part of the sodium carbonate requirements of the high temperature conversion operation.

Within mixer 20 the finely divided cell lining material is thoroughly admixed with the sodium carbonate added thereto. Following the solids mixing operation the resulting, substantially homogeneous admixture of cell lining material and sodium carbonate is supplied via line 21 to high temperature conversion or roasting zone or roaster 22.

Roaster 22 may comprise any suitable means or apparatus for effecting high temperature contact between a gas, such as an oxygen-containing gas, e.g. air, and the solids admixture supplied via line 21. Roaster 22 may be a batch type roaster or continuously operating type roaster, such as a rotating kiln or multihearth rabble arm roaster of the Herreshof type. Preferably roaster 22 is a Herreshof type roaster, the solids rabbling contact afforded therein serving to promote good solid-solid contact between the soda carbonate and the cell lining material and also between the oxygen-containing gas, air, supplied from a suitable source, not shown, via line 24 and the carbon or carbonaceous material in the cell lining material. Further, by use of a Herreshof type furnace or roaster, temperature control during the high temperature conversion or roasting operation can readily be effected by bleeding air into the furnace or by by-passing the furnace gases around any hearth. Temperature control during the roasting operation is desirable since cell lining material varies greatly as to carbon or carbonaceous material content. It is obvious, however, as indicated that many other types of roasters or kilns can be employed provided these are effective to provide a high temperature environment for the sodium carbonate and cryolite undergoing reaction.

Because of the relatively high carbon content of the cell lining material and also because the high temperature conversion or roasting operation involving the reaction between cryolite and the sodium carbonate yields carbon dioxide, the roaster off gases removed from roaster 22 via line 25 contain a substantial amount of gaseous carbon dioxide, about 20% by volume, more or less. The amount of carbon dioxide therein can be varied to some extent depending upon the amount of air supplied via line 24 to roaster 22 and the carbon content of the cell lining material undergoing treatment.

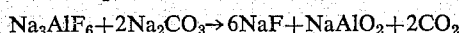
During the roasting operation, by controlling the amount of sodium carbonate added via line 21 to roaster 22 in admixture with the cell lining material, the amount of alumina, derivable from the cryolite in the cell lining material, rendered soluble can be regulated so as to control the resulting recovered cryolite product purity. In the roasting operation if there is a deficiency of sodium carbonate the free energy change favors the formation of sodium fluoride rather than sodium aluminate in accordance with the following chemical equation:



The resulting formed alumina, however, because it has been heated to a high temperature during the roasting

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operation, is essentially water-insoluble and insoluble in dilute caustic and therefore cannot contaminate the cryolite recovered as product in the subsequent cryolite precipitation operation. Normally, alumina sufficient to provide a weight ratio of $\text{Al}_2\text{O}_3:\text{F}$ of about 0.45 in the cryolite precipitator or in the solution from which the cryolite is precipitated, is desired. Therefore, the amount of soda or sodium carbonate in the process will generally be in excess of that needed for the fluoride only and the reaction in roaster 22 will proceed in accordance with the chemical equation:



An excess of alumina can easily be added when processing ordinary cell lining material by adding more sodium carbonate and this may be desirable if auxiliary sources of fluoride or fluorine-containing materials, such as scrubber solutions from hydrogen fluoride or aluminum fluoride plants or aluminum smelters, are available and employed for the recovery of fluoride values therefrom, or sodium fluoride obtained from fluosilicate is available.

The effect of the amount of added sodium carbonate during the roasting operation upon the solubility of fluoride-containing materials and alumina is graphically illustrated in accompanying FIG. 2. Accordingly, as indicated in FIG. 2 the weight ratio of alumina to fluorine in the precipitator solution can be varied in accordance with the amount of sodium carbonate added in the solids admixture supplied via line 21 to or present within roaster 22.

Scrubber solids are obtainable during the electrolytic refining of aluminum by collecting the material volatilized from the cell, particularly at the anode, by water scrubbing. The scrubber solutions may be utilized in the process of this invention and are conveniently utilized therein by being supplied from a suitable source, not shown, via line 28 to filter 29 for the removal of the solids therefrom. The resulting filtered solids are withdrawn from filter 29 via line 30 and supplied via line 30 into mixer 20 for admixture with the crushed and finely ground cell lining material therein.

Cell lining material and scrubber solids normally contain about 12–30% by weight carbon. When these materials are roasted in admixture with sodium carbonate in roaster 22 to convert the cryolite therein to water-soluble sodium aluminate and sodium fluoride at an elevated temperature, such as at least above about 500° C., the carbon therein is burned. This result is highly desirable because the heat so liberated, about 1600–4000 B.t.u. per pound of cell lining material, helps to maintain the elevated temperature within roaster 22 needed to effect the sodium carbonate-cryolite reaction and to evaporate any spent liquor which may be supplied or recycled to roaster 22, such as with the sodium carbonate slurry supplied to mixer 20 via line 31. The burning of the carbon or carbonaceous material in the cell lining material within roaster 22 also advantageously serves to reduce the total amount of solids to be handled in the subsequent leaching operation for the recovery of the water-soluble roaster reaction products, sodium fluoride and sodium aluminate.

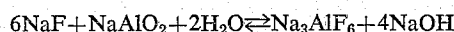
The roaster product recovered from roaster 22 via line 26 is generally a white, friable powder which requires no grinding before leaching and it can be readily cooled by being supplied or added directly via line 26 to the leaching circuit or leaching tank 32 for the dissolution of the water-soluble sodium fluoride and sodium aluminate therefrom.

It has been found that the roasted product from roaster 22 is very easily and rapidly leached free of soluble fluoride and that the insoluble solids therein readily and rapidly settle and are easily filtered. There is no gas formation or foaming problem presented during the leaching operation. The aluminum metal, aluminum carbide and aluminum nitrides and other relatively surface active materials which tend to make a stable foam

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in the conventional aqueous caustic cryolite recovery process are destroyed by reaction with air, sodium carbonate and/or water within roaster 22. Water-soluble cyanides which sometimes present a problem in the conventional caustic cryolite recovery process are also destroyed within roaster 22.

Within leaching circuit or leaching tank 32 the water-soluble materials in the roaster product are dissolved, the sodium fluoride and sodium aluminate in roaster product dissolving in the aqueous solution supplied to leaching tank 32 via line 34. Although sodium fluoride and sodium aluminate are water-soluble, they tend to react to form cryolite in the resulting solution within leaching tank 32 in accordance with the following chemical equation:



The resulting formed cryolite tends to precipitate, particularly when the leaching solution approaches saturation with respect to the sodium fluoride and/or the temperature of the leaching solution falls below about 50° C. Accordingly, it is desirable to maintain the aqueous leaching solution within leaching circuit or leaching tank 32 relatively hot, e.g. above about 50° C. It has been found, however, that the addition of sodium hydroxide, which may be added to leaching tank 32 in the form of a concentrated (e.g. 50% by wt.) aqueous solution via line 35 in an amount of about 2 grams per liter based on the leaching solution, i.e. below about 1% by weight based on the leaching solution, effectively prevents the precipitation of cryolite during the leaching operation. Generally, the higher the concentration of alumina in the resulting leaching solution, the greater the need for the added sodium hydroxide therein.

Following the leaching operation within leaching tank 32 the leached solids are supplied via line 36 to washing circuit or washing tank 38 wherein the leached solids are washed with fresh wash water supplied to washing tank 38 from a suitable source, not shown, via line 39. The resulting wash water or overflow from washing tank 38 is supplied via line 34 to leaching tank 32 to dissolve the water-soluble fluorides and sodium aluminate from the roaster product solids supplied thereto via line 26.

Because most or all of the carbon has been removed from the roaster product, thereby reducing the amount of solids being handled and leached within leaching tank 32, and because of the excellent settling and filtering characteristics exhibited by the insoluble solids of the roaster produce being leached within leaching tank 32, it has been found that the recovery of water-soluble fluoride from the roaster product is improved. Specifically, it has been observed that in the cryolite recovery operation in accordance with this invention the water-soluble fluorine in the tailings, recovered from washing tank 38 via line 40, does not exceed 3% of the available water-soluble fluorine in the cell lining feed material whereas in the conventional caustic cryolite recovery process, the amount of soluble fluoride in the tailings amounts to about 4–5% of the total in the feed. The tailings recovered from washing tank 38 via line 40 contain up to 80% by weight alumina and if a red mud lime-soda sinter plant is operated nearby the alumina in these tailings can readily be utilized to commercial advantage.

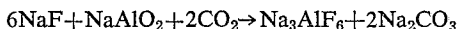
The leaching circuit 32 and/or the washing circuit 38 may comprise a number of thickeners, filters or centrifuges or equivalent solids-liquids concentrating and/or separating devices. Concurrent or countercurrent operation of the leaching and/or washing circuit may be employed but the countercurrent operation for both leaching and washing is preferred in the practice of this invention to reduce dilution. Further, it is preferred to leach and wash at temperatures close to the boiling point of the leaching and washing solutions but this is not essential. In actual practice, it has been found possible to reach a concentration of 15 g.p.l. (grams per liter) water-

soluble fluoride in the leaching circuit overflow in line 41 while at the same time effecting at least 97% solution of the available caustic-soluble fluoride in the cell lining feed material, such as may be supplied to the process via line 10.

The resulting solution or overflow from leaching circuit 32 is withdrawn therefrom via line 41 and supplied to surge tank 42 which is also, if desired, supplied with the filtrate of the scrubber slurries obtained from filter 29 via line 44. Because of the fluctuations in the fluoride and sodium carbonate contents of the cell lining material being processed the retention time of the liquids within surge tank 42 should be about three times the roaster retention time with good mixing. Desirably, the liquid within surge tank 42 is sampled and analyzed frequently. If the alumina to fluorine weight ratio therein is too low the sodium carbonate content in the feed supplied to roaster 22 via line 21, or present within roaster 22, should be increased. If the ratio is too high the sodium carbonate should be decreased. This control is desirable so that a reasonably high grade of recovered cryolite will be produced at all times.

The liquid in surge tank 42 is supplied via line 45 to first stage cryolite precipitation or precipitator 46 wherein the liquid is contacted with the gaseous carbon dioxide in the roaster off gases recovered from roaster 22 via line 25 after having passed through evaporator 48 and then to first stage precipitator 46 via lines 49 and 50. It is thus seen that the carbon dioxide generated within roaster 22 by the oxidation of the carbonaceous material therein and generated by the reaction between the sodium carbonate and the cryolite in the cell lining material therein is advantageously recovered and employed to effect the precipitation and regeneration of cryolite from the water-soluble sodium fluoride and sodium aluminate supplied to precipitator 46 in the liquid overflow via line 41.

Within precipitator 46 cryolite is formed by reaction between carbon dioxide and sodium fluoride and sodium aluminate in accordance with the following chemical equation:



The material from first stage precipitator 46 is then supplied via line 51 to thickener 52 wherein a portion of the aqueous sodium carbonate-containing solution or spent liquor recovered via line 54 is supplied, if desired, via line 55 to leaching circuit 32. In actual practice the spent liquor thus recycled via line 55 to leaching circuit 32 contains about 3 grams per liter fluorine. The reason for the recycle of the partially spent liquor in line 55 to leaching circuit 32 is to reduce the water intake in the overall process and to reduce the evaporator requirements. This recycle also serves to raise the sodium carbonate content in the spent liquor returned to the roaster such as via line 31 from evaporator 48.

The cryolite-containing slurry is removed from thickener 52 via line 56 and passed to filter 58 for the separation of the cryolite therefrom. The resulting separated cryolite is then passed via line 59 to dryer 60 and the resulting dried product recovered therefrom via line 61.

The filtrate from filter 58 is supplied via line 62, together with the remaining portion of the partially spent liquor removed from thickener 52 via lines 54 and 64, to second stage precipitator 65 wherein it is contacted with gaseous carbon dioxide supplied via line 49. Second stage cryolite precipitation or second stage precipitator 65 is employed to effect substantially complete recovery of all the available cryolite from the raw material supplied to the process.

The slurry from second stage precipitator 65 is passed via line 66 to thickener 68 for the removal of solids therefrom which are returned via line 69 to first stage precipitator 46. The resulting spent liquor is recovered from thickener 68 via line 70 and is advantageously re-

cycled to the process as the spent liquor supplied to ball mill 14 via line 15 or as the liquid employed as the scrubbing liquid in the production of scrubber slurries supplied to filter 29 via line 23 or the spent liquor may be supplied directly via line 71 to evaporator 48 for concentration of sodium carbonate therein and the production of the sodium carbonate slurry supplied via line 31 to mixer 20, or the spent liquor may be supplied directly, without concentration, to mixer 20 or to roaster 22 for temperature control therein, all as indicated in FIG. 1 of the drawings.

As indicated hereinabove the cell lining material may contain as much as about 3% by weight sodium hydroxide and as much as about 10% by weight sodium carbonate. In the conventional caustic cryolite recovery process the sodium carbonate present in the cell lining material is inert. However, in the cryolite recovery process in accordance with this invention involving roasting the cryolite-containing cell lining material in the presence of sodium carbonate, both the sodium hydroxide and the sodium carbonate react substantially quantitatively with the cryolite to form water-soluble sodium fluoride and water-soluble sodium aluminate. Because of this the sodium ion intake of the process of this invention is substantially less than that of the conventional caustic cryolite recovery process and therefore the spent liquor bleed is substantially less and fluorine losses in the spent liquor are, accordingly, substantially reduced. Further, by evaporating part of the spent liquor all the sodium carbonate necessary for continuous operation of the subject process can be provided by the cell lining material itself, with sufficient surplus for scrubber operations if desired. Further, if another need for spent liquor presents itself it may even be more desirable or more economical to purchase dry soda ash (sodium carbonate) rather than to evaporate the spent liquor for the concentration and recovery of sodium carbonate therein.

It is seen, therefore, that by following the practices of this invention a superior and improved process is provided for the recovery of cryolite from cryolite-containing used carbonaceous cell lining material and solids collected from the gases escaping from the cell, particularly as compared with the conventional cryolite recovery process employing aqueous caustic. More specifically, the subject sodium carbonate high temperature sintering or roasting process possesses the following advantages over the conventional caustic cryolite recovery process:

(1) Fluorine recovery is increased from about 87% to about 93% of the available fluorine in the cell lining material.

(2) The amount of process sodium hydroxide is reduced to about 10% of that required in the conventional caustic cryolite recovery process.

(3) By-product sodium carbonate produced in the precipitators can be employed directly to treat the cell lining material without an intermediate causticizing, and make-up sodium carbonate is provided by the sodium carbonate present in the cell lining material itself.

(4) The sodium ion intake in the subject process is reduced by as much as 40%, thereby affording a correspondingly, smaller spent liquor bleed.

(5) Good control of the fluorine to alumina ratio in the overflow liquor supplied to the cryolite precipitator is available, thereby making possible the production of a consistent, higher grade recovered cryolite product.

(6) The tailings to be disposed of are reduced in weight by as much as 30%.

(7) The leaching operation for the recovery of the water-soluble sodium fluoride and water-soluble sodium aluminate from the roasted product is easily carried out, is substantially trouble-free and requires smaller tankage. The insoluble portion of roasted product settles and

filters readily and there is no foaming during the leaching operation.

The advantages of employing the subject sodium carbonate high temperature conversion or roasting process over the conventional caustic cryolite recovery process are further indicated in accompanying Table II.

TABLE II

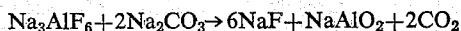
Comparison Between Conventional Caustic Cryolite Recovery Process and Subject Sodium Carbonate Roast Process

	Caustic Process	Soda Roast Process
Potlining to process.....lbs..	100.0	100.0
Total available fluorine.....lbs..	16.3	16.3
NaOH in potlining.....lbs..	3.0	3.0
NaOH added.....lbs..	22.8	2.0
Na ₂ CO ₃ in potlining.....lbs..	7.0	7.0
Na ₂ CO ₃ added.....lbs..		8.2
Na ₂ CO ₃ in spent liquor.....lbs..	46.2	28.2
Leach residue.....lbs..	60.0	40.6
CO ₂ required.....lbs..	31.3	20.7
100% cryolite produced.....lbs..	22.4	24.0
Grade of cryolite.....percent..	85	90

As will be apparent to those skilled in the art in the light of the foregoing disclosure, many modifications, alterations or substitutions are possible in the practice of this invention without departing from the spirit or scope thereof.

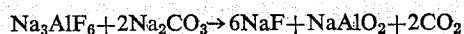
We claim:

1. A method of recovering cryolite values from the carbonaceous cell lining of an electrolytic cell employed in the electrolytic refining of aluminum which comprises roasting an admixture consisting essentially of cryolite-containing cell lining material in the presence of added water-soluble carbonate selected from the group consisting of sodium carbonate and sodium bicarbonate, said roasting operation being carried out in the presence of a stoichiometric excess of said water-soluble carbonate and at an elevated temperature and for a period of time sufficient to react substantially all of the cryolite in said carbonaceous cell lining material with said carbonate with the resulting formation of sodium fluoride and sodium aluminate in accordance with the chemical equation



contacting the resulting reaction admixture containing sodium fluoride and sodium aluminate with an aqueous solution to dissolve said sodium fluoride and said sodium aluminate therefrom, reacting the resulting aqueous solution with carbon dioxide to precipitate cryolite therefrom and recovering the resulting precipitated cryolite.

2. A method of recovering cryolite values from cryolite-containing carbonaceous cell lining material which comprises roasting an admixture consisting essentially of said carbonaceous cryolite-containing material with added soda carbonate, said roasting operation being carried out in the presence of a stoichiometric excess of sodium carbonate and at an elevated temperature and for a period of time sufficient to react substantially all of the cryolite therein with sodium carbonate with the resulting formation of sodium fluoride and sodium aluminate in accordance with the chemical equation



contacting the resulting reaction admixture with an aqueous solution to dissolve sodium fluoride and sodium aluminate therefrom, contacting the resulting aqueous solution with carbon dioxide to precipitate cryolite therefrom

together with the formation of sodium carbonate, separately recovering the precipitated cryolite and employing the sodium carbonate contained in the aforesaid aqueous solution to react with additional carbonaceous cryolite-containing material for the recovery of cryolite therefrom.

3. A method in accordance with claim 2 wherein said aqueous solution employed to dissolve the sodium fluoride and sodium aluminate from the reaction admixture contains a minor amount of sodium hydroxide dissolved therein sufficient to inhibit the precipitation of cryolite therefrom during the aforesaid dissolution operation.

4. A method of recovering cryolite from carbonaceous cryolite-containing cell lining material employed in the electrolytic refining of aluminum which comprises reducing said cryolite-containing cell lining material to particle form, roasting an admixture consisting essentially of the resulting particle from cell lining material in the presence of an added water-soluble carbonate selected from the group consisting of sodium bicarbonate and sodium carbonate, said roasting operation being carried out in the presence of a stoichiometric excess of said water-soluble carbonate and at a temperature in the range 500-900° C. and for a period of time sufficient to form sodium fluoride and sodium aluminate with substantially all of the cryolite in said cell lining material in accordance with the equation $\text{Na}_3\text{AlF}_6 + 2\text{Na}_2\text{CO}_3 \rightarrow 6\text{NaF} + \text{NaAlO}_2 + 2\text{CO}_2$, leaching the resulting reaction mixture with an aqueous solution to dissolve sodium fluoride and sodium aluminate therefrom, subjecting the resulting leached reaction mixture to washing with water to yield the aforesaid aqueous solution, contacting the resulting aqueous solution recovered from the aforesaid leaching operation, now containing sodium fluoride and sodium aluminate dissolved therein, with gaseous carbon dioxide to precipitate cryolite therefrom and separating the resulting precipitated cryolite.

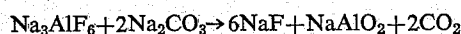
5. A method in accordance with claim 4 wherein said leaching operation is carried out in the presence of dissolved caustic in an amount of about 2 grams NaOH per liter of aqueous solution.

6. A method in accordance with claim 4 wherein at least a part of said gaseous carbon dioxide employed to precipitate cryolite is obtained by the oxidation of the carbonaceous material in said carbonaceous cell lining material during said roasting operation.

7. A method in accordance with claim 4 wherein said water-soluble carbonate is sodium bicarbonate.

8. A method in accordance with claim 4 wherein said water-soluble carbonate is sodium carbonate.

9. A method of recovering cryolite values from carbonaceous, cryolite-containing cell lining material of an electrolytic cell employed in the electrolytic refining of aluminum which comprises, reducing said carbonaceous cryolite-containing cell lining material to particle form in the presence of aqueous spent liquor containing sodium carbonate dissolved therein; separating the resulting reduced cell lining material from said spent liquor, admixing added sodium carbonate with the resulting reduced cell lining material to yield an admixture containing a stoichiometric excess of sodium carbonate, subjecting the resulting admixture consisting essentially of reduced cell lining material and sodium carbonate to roasting at an elevated temperature in the range 500-900° C. for a period of time sufficient to effect reaction between the sodium carbonate in said admixture and substantially all of the cryolite contained in said cell lining material in said admixture in accordance with the equation



subjecting the resulting reaction admixture now containing sodium fluoride and sodium aluminate to contact with an aqueous solution to dissolve said sodium fluoride and said sodium aluminate therefrom, contacting the resulting

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solution containing sodium fluoride and sodium aluminate dissolved therein with carbon dioxide to precipitate cryolite therefrom and to yield a resulting spent liquor containing sodium carbonate dissolved therein, separating the resulting precipitated cryolite and employing said resulting spent liquor as the aforesaid first mentioned spent liquor to contact additional said cell lining material.

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