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(54) Titre : PROCÉDE POUR LE RECYCLAGE DE BRASQUES USEES (SPL) PROVENANT DE LA PRODUCTION D'ALUMINIUM PRIMAIRE  
 (54) Title: PROCESS FOR RECYCLING SPENT POT LININGS (SPL) FROM PRIMARY ALUMINIUM PRODUCTION

(57) **Abrégé/Abstract:**

The present invention relates to a process for recycling SPL (spent pot linings), from primary aluminium production, comprising the steps of grinding the separated fractions or cuts, separating materials by means of mechanical treatment, mixing salt slags with SPL, dissolving in water the product obtained in the previous step, carrying out a chemical reaction between water and the materials to be made inert, sedimenting, removing cyanides, filtering to obtain a soluble fraction and another insoluble fraction, washing the insoluble fraction, crystallizing salts of the soluble fraction and aging or conditioning the insoluble fraction. The present invention further relates to the product obtained by means of said process and the use thereof as new material in different fields of industry.



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(54) Title: PROCESS FOR RECYCLING SPENT POT LININGS (SPL) FROM PRIMARY ALUMINIUM PRODUCTION

(57) Abstract: The present invention relates to a process for recycling SPL (spent pot linings), from primary aluminium production, comprising the steps of grinding the separated fractions or cuts, separating materials by means of mechanical treatment, mixing salt slags with SPL, dissolving in water the product obtained in the previous step, carrying out a chemical reaction between water and the materials to be made inert, sedimenting, removing cyanides, filtering to obtain a soluble fraction and another insoluble fraction, washing the insoluble fraction, crystallizing salts of the soluble fraction and aging or conditioning the insoluble fraction. The present invention further relates to the product obtained by means of said process and the use thereof as new material in different fields of industry.

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**PROCESS FOR RECYCLING SPENT POT LININGS (SPL) FROM PRIMARY  
ALUMINIUM PRODUCTION**

**Object of the Invention**

5           The present invention describes a process for recycling used electrolytic cells or spent pot linings (SPL) from primary aluminium production. Said recycling is carried out in a plant for recycling the salt slags from the rotary furnaces of an aluminium refinery.

          The invention is comprised in the technical field of metallurgy, and specifically in the field of exploiting and using metal materials.

10 **Background of the Invention**

          SPL is a well known waste resulting from the aging of used electrolytic cell cathodes in primary aluminium production. This cathode is formed from refractory material, conductive carbonaceous material and other various materials (iron bars, insulators, etc.). Over the operating time, these materials react with the content of the  
15 tanks and effectiveness in their operation is lost, and they must be disassembled.

          A toxic and hazardous waste, SPL, is thus obtained which is normally poured in to special dumps, as such, or after some impurities have been removed. This waste has several characteristics, depending on the cut made when disassembling the lining from the used cathodes: refractory, carbon or mixed. CN<sup>-</sup>, nitrides, carbides, fluorine,  
20 etc, are the most important impurities.

          Due to the toxicity of this waste, the government must control the treatment and destination of this material in order to not affect the environment. The carbonaceous part has the most evident application for power production, but must also be prepared.

          SPL is generally treated in dry or wet conditions to destroy the most harmful  
25 impurities, obtain an inert waste, or separate and reuse any of its present constituents.

          To date, there are many different processes for inerting, recycling and reusing the material from these cathodes, however, most of them are focused on reducing or preventing the hazard involved in handling the powdery waste, and are focused on adding some type of substance with passivating properties reducing the hazard.

30           In this same sense, patent US5352419 describes a process for the recovery of aluminium and fluorides from SPL comprising the steps of calcining SPL to produce an ash with environmentally acceptable levels; the ashes are subsequently filtered in a solution containing a mineral acid, obtaining the corresponding aluminum salt in a sufficient amount to dissolve the aluminum and fluoride contents, in order to  
35 subsequently subject the filtered liquid to hydrolysis to cause precipitation of an

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aluminum fluoride product.

European patent EP0550136 describes a method for the treatment of SPL, including refractory materials, to transform SPL into a state in which it can be used as a filler material or as raw material. The SPL is crushed and supplied to an electrothermic smelting furnace, optionally together with a SiO<sub>2</sub> source, in which the SPL is melted at a temperature between 1300 and 1750°C. An oxidizing agent is supplied to the melt to oxidize carbon and other oxidizable components contained in the SPL such as metals, nitrates and carbides. A calcium oxide source is also supplied to the smelting furnace in the amount necessary to react with all the fluorides present in the form of CaF<sub>2</sub>, the slag of which is liquid at the bath temperature inside the furnace. The calcium aluminate slags, or the calcium aluminate silicate slags and, optionally a metal phase, are used for blocks and granules.

Patent US6132574 relates to a bottom lining for electrolytic cells, especially for electrolytic cells of aluminium from primary production and from secondary refining, the base body of the electrolytic cells being formed by steel pots, as well as a process for manufacturing it.

All the previous patents have attempted to recover certain substances contained in SPL and produce an inert waste which can be poured without problems. To that end, pilot and industrial plants have been built to carry out the operations for that purpose. However, the investments to be made are very large, the process for treating SPL was very complex, the waste obtained was not as inert as expected, and the products obtained did not have the desired quality. It is therefore necessary to develop new processes or routes for eliminating or treating SPL with lower associated costs and in which good results as regards inerting and clarity are obtained in order to affect the environment to the lowest extent possible.

#### Description of the Invention

In accordance with one aspect of the present invention, there is provided a process for recycling SPL (spent pot lining) from primary aluminium production, wherein the SPL consists of a fraction or cut based on conductive carbonaceous materials and another fraction or cut based on refractory materials, iron bars and insulators from the disassembling of lining, which are ground and separated by means of mechanical treatment and magnetic systems, wherein the process comprises the following steps:

- i. mixing salt slags from refineries for recycling aluminum slags with SPL at a temperature within the range from 90 to 95°C to obtain a mixture of salt slag-SPL;

- ii. dissolving the mixture of salt slag-SPL in water, at a pH within the range from 11 to 12 and carrying out a chemical reaction between water and said mixture for obtaining a dissolution;
- iii. sedimenting said dissolution;
- iv. eliminating cyanides from the dissolution by adding sodium hypochlorite;
- v. filtering to obtain a soluble fraction and another insoluble fraction;
- vi. washing the insoluble fraction obtained in the previous step;
- vii. crystallizing salts of the soluble fraction by means of evaporation;  
and
- viii. aging or conditioning the insoluble fraction.

In accordance with a further aspect of the present invention, there is provided a process for recycling SPL (spent pot lining) from primary aluminium production, wherein the SPL consists of a fraction or cut based on conductive carbonaceous materials and another fraction or cut based on refractory materials, iron bars and insulators from the disassembling of lining, which are ground and separated by means of mechanical treatment and magnetic systems, wherein the process comprises the following steps:

- i. mixing salt slags from refineries for recycling aluminum slags with SPL at a temperature within the range from 90 to 95°C to obtain a mixture of salt slag-SPL and maintaining the mixture at said temperature;
- ii. dissolving the mixture of salt slag-SPL in water, at a pH within the range from 11 to 12 and carrying out a chemical reaction between water and said mixture for obtaining a dissolution;
- iii. sedimenting said dissolution;
- iv. eliminating cyanides from the dissolution by adding sodium hypochlorite;
- v. filtering to obtain a soluble fraction and another insoluble fraction;
- vi. washing the insoluble fraction obtained in the previous step;
- vii. crystallizing salts of the soluble fraction by means of evaporation;  
and
- viii. aging or conditioning the insoluble fraction.

In accordance with a further aspect of the present invention, there is provided a product obtained by means of the process as described above, which comprises the following elements:  $\text{Al}_2\text{O}_3$ ;  $\text{SiO}_2$ ;  $\text{CaF}_2$ ;  $\text{Fe}_2\text{O}_3$ ; cryolite;  $\text{MgO}$ ; and carbon which are respectively in the following proportions: 55-60, 8-15, 2-8, 0.8-2, 0-5, 3-5 and 2-10.

In accordance with a further aspect of the present invention, there is provided use of a product obtained by means of the process as described above for construction, for its use in ceramic materials and artificial mineral fibers.

The present invention describes a process for recycling SPL from primary aluminium production, in which inert products with a higher quality are obtained compared to that described in the state of the art. Said process is implemented in existing plants for the treatment of salt slags from a rotary furnace used in aluminium refineries for recycling aluminium slags. Hazardous toxic waste (HTW) such as salt slags, combustion furnace filter dust and slag grinding dust for example, are treated in these plants. Each material, either salt slags, aluminium slag dust, filter dust or the object of the invention, SPL, are treated by means of an equivalent process, although the suitable specific parameters are adjusted for each of them.

Thus, by way of example, for salt slags, the main operations that are carried out are grinding, dissolution, reaction, sedimentation, filtering, washing, crystallization and maturing or drying. The waste is supplied to this circuit at the most suitable point, before or in the reactor. For the aluminium slag dust from grinding, there is dosing, dissolution and reaction in another reactor. The mixture then goes to the main circuit. For filter dust, a special conveyor, pyrolysis if necessary, and dosing are used, the material then going to the main circuit before the reaction.

For the SPL object of the present invention, the process comprises the following steps:

- 10 a) Grinding each of the separated fractions or cuts.
- b) Mechanically treating in order to separate materials. Said separation treatment is carried out by sizes, by means of mesh type sieves and also by means of magnetic systems for separating iron particles.
- c) Mixing salt slag with SPL in a 3:1 ratio. Mixing in this ratio is mainly due to the fact that a salt slag/SPL mixture at a different ratio has different reactivity, and requires different external actions for maintaining 90-95°C in the reactor.
- 15 d) A solution is made with the product resulting from the previous step in water at a basic pH, preferably a pH within the range from 11 to 12.
- e) A chemical reaction is carried out, the small amounts of aluminium, nitrides, carbides and sulfides are thus eliminated and the corresponding gases are also given off. The toxic materials are thus eliminated or made inert. The reaction is carried out between the hot water at a basic pH and the components to be made inert. Said reaction is carried out in closed reactors with an inert (oxygen-free) atmosphere, with stirring. In these reactions, the gases are aspirated to the gas treatment plant already existing in salt slag treatment plants.
- 20 f) Sedimenting and eliminating cyanides. This elimination is carried out by means of adding sodium hypochlorite according to the amount of cyanide in the solution.
- g) Filtering and washing. To separate the soluble and insoluble fractions and wash the latter by means of traditional filterings described in the state of the art.
- 30 h) The salts of the soluble fraction are crystallized by means of water evaporation by any technique comprised in the state of the art, preferably by means of heating. Flux salts with small amounts of fluorine are thus obtained, which improves the type of salt usually obtained in these types of plants (salt slags). Therefore, a salt is thus obtained which is a better fluxing agent than the salts obtained by other processes.
- 35 i) The insoluble fraction is aged or conditioned by means of analyzing the

components and dehydrating by decanting.

The main differences while treating SPL in relation to the treatment of salt slags are:

- 5 - In the grinding, the SPL material is less hard and the dwell time of the material in the installation is much shorter. Internal recycling thereof in a closed circuit is not required.
- In the subsequent separation of materials, SPL contains less Al and more C, therefore the equipment must be regulated in a different manner. The equipment works with a less strict regulation in Al and Fe separators.
- 10 - The dissolution of SPL hardly presents any difficulty and requires less water than usual with salt slags.
- As regards the reactivity, it must be taken into account that SPL is less reactive. It has been considered that the ideal working ratio is mixing slag/SPL in a 3:1 ratio. SPL does not have sufficient reactivity to start the reaction and it is therefore necessary to mix it with salt slags in that ratio.
- 15 - In the gases obtained from the reaction, the same types of gases are produced with the presence of SPL with some differences: there is a greater CH<sub>4</sub> production.
- In the liquor to be handled, with SPL there is more fluorine and there are cyanides.
- 20

The most important differences of the treatment of SPL in relation to the treatment of salt slags is in the reaction with water of both of them.

With 100% SPL, external heating is required and there are more than 100 ppm of cyanides in the liquor obtained; these cyanides must be eliminated with the addition of sodium hypochlorite according to the reactions:



This is not necessary when operating only with salts slags or aluminium slags, having only 2 ppm of cyanides. Tests also show that a liquor with 800 ppm of F is obtained.

A salt slag /SPL mixture at a different ratio will have different reactivity and requires different external actions to maintain 90-95°C in the reactor. Since SPL has 4 times more F, working with 25/75% of SPL/salt slag is proposed so as to have fluorine in the liquor in the order of 100 ppm in the liquor and so that the level of this element does not increase significantly in the final oxide obtained.

When the process is carried out, it produces an insoluble solid product, as well as salts the produced quality of which has additional fluorine, making them a better product as a fluxing agent with respect to those obtained by treating salt slags.

5 A second fundamental aspect of the present invention relates to the insoluble product obtained by means of the previously described process which is characterized in that it is an inert material in which the main component is aluminium oxide ( $\text{Al}_2\text{O}_3$  in a proportion of 55-60), and in a non-limiting sense, other metal oxides ( $\text{SiO}_2$  in a proportion of 8-15,  $\text{F}_2\text{Ca}$  in a proportion of 2-8,  $\text{Fe}_2\text{O}_3$  in a proportion of 0.8-2, cryolite in a proportion of 0-5 and  $\text{MgO}$  in a proportion of 3-5), carbon (in a proportion of 2-10),  
10 having applications as secondary raw material, substituting natural raw materials which can be used up or are non-renewable.

A third fundamental aspect of the present invention relates to the use of the previously defined product for construction, for its use in ceramic materials, artificial mineral fibers, etc.

#### 15 Preferred Embodiment of the Invention

In the Befesa Salt Slag plant in Witchurch (Wales) in which aluminium and salt slags are recycled, 25 tn. of SPL were recycled. The installation was fed a 3:1 salt slag/SPL ratio. 100 tn. of mixture in total were treated and the ground material was collected in a separate bin. The reaction also took place in a reactor dedicated to this  
20 material and the liquor obtained was kept separated. At the end, 100 tn. of a solid aluminium oxide product, without a considerable increase of F, were obtained.

The embodiments of the present invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for recycling SPL (spent pot lining) from primary aluminium production, wherein the SPL consists of a fraction or cut based on conductive carbonaceous materials and another fraction or cut based on refractory materials, iron bars and insulators from the disassembling of lining, which are ground and separated by means of mechanical treatment and magnetic systems, wherein the process comprises the following steps:
  - i. mixing salt slags from refineries for recycling aluminum slags with SPL at a temperature within the range from 90 to 95°C to obtain a mixture of salt slag-SPL and maintaining the mixture at said temperature;
  - ii. dissolving the mixture of salt slag-SPL in water, at a pH within the range from 11 to 12 and carrying out a chemical reaction between water and said mixture for obtaining a dissolution;
  - iii. sedimenting said dissolution;
  - iv. eliminating cyanides from the dissolution by adding sodium hypochlorite;
  - v. filtering to obtain a soluble fraction and another insoluble fraction;
  - vi. washing the insoluble fraction obtained in the previous step;
  - vii. crystallizing salts of the soluble fraction by means of evaporation; and
  - viii. aging or conditioning the insoluble fraction.
2. The process for recycling SPL from primary aluminium production according to claim 1, wherein the salt slags are mixed with SPL at a 3:1 ratio.
3. The process for recycling SPL from primary aluminium production according to claim 1, wherein in the chemical reaction, nitrides, aluminium, carbides and sulfides are eliminated and gases are also given off.
4. The process for recycling SPL from primary aluminium production according to any one of claims 1 to 3, wherein the reaction is carried out in closed reactors with an inert atmosphere with stirring.
5. The process for recycling SPL from primary aluminium production according to any one of claims 1 to 4, wherein the crystallization is carried out by means of evaporation by heating.

6. The process for recycling SPL from primary aluminium production according to claim 1, wherein the aging is carried out by means of analyzing the components and dehydrating by decanting.

7. A product obtained by means of the process according to claim 1, which comprises the following elements:  $\text{Al}_2\text{O}_3$ ;  $\text{SiO}_2$ ;  $\text{CaF}_2$ ;  $\text{Fe}_2\text{O}_3$ ; cryolite;  $\text{MgO}$ ; and carbon which are respectively in the following proportions: 55-60, 8-15, 2-8, 0.8-2, 0-5, 3-5 and 2-10.

8. The product according to claim 7, which is insoluble.

9. Use of a product obtained by means of the process according to claim 1 for construction, for its use in ceramic materials and artificial mineral fibers.