PATENT REVIEW OF RED MUD TREATMENT – PRODUCT OF BAYER PROCESS

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PREHLAD PATENTOV O SPRACOVANI CERVENEHI KALU Z BAYEROVHO SPOSOBU VYROBY AL_2O_3

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Abstract

V každom technologickom procese výroby kovov vznikajú medziprodukty v rôznej forme. Tieto medziprodukty môžu byť v pevnom, kvapalnom alebo plynnom skupenstve. Skládkovanie medziproduktov môže predstavovať ekonomický problem (vysoké prevádzkové náklady skládkovania) ale tiež aj ekologický problém (možný únik nebezpečných látok do prostredia). To je hlavný dôvod veľkej snahy ekonomicky spracovať takéto medziprodukty a recyklovať užitočné zložky v nich obsiahnuté. Červený kal je jedným z takýchto medziproduktov z výroby oxidu hlinitého. Vysoká produkcia oxidu hlinitého znamená vysokú produkciu červeného kalu. Priemysel oxidu hlinitého celosvetovo vyprodukuje viac ako 70 miliónov ton červeného kalu ročne. Tento literárny prehľad je zameraný na patentovú literatúru, s cieľom sumarizovať patenty venované problematike spracovania červeného kalu. Zahŕňa v sebe 88 patentov z celého sveta vydaných v období rokov 1957 až 2002. Len niekoľko zo spomenutých patentov, ktorých cieľom bolo spracovanie červeného kalu z výroby oxidu hlinitého, má v súčasnosti využitie, aj to iba čiastkové. Hlavným dôvodom je slabá ekonomika spracovania červeného kalu vo všeobecnosti. Väčšina zo súčasných patentov v sebe zahŕňa niekoľko rozličných postupov spracovania červeného kalu. Jedná sa o spracovanie červeného kalu priamym kontaktom s pevným, kvapalným alebo plynným reaktantom a následným hydrometalurgickým, tepelným alebo iným druhom spracovania.

Abstract

By-products in different form are produced in each technological process of metal production. They can be in the solid, liquid or gas form. The by-product disposal could signify economical (high-cost dump maintenance) but also ecological problem (possible escape of dangerous materials to the environment). Therefore, there is a big effort for treatment and recycling of valuable components of such by-products. The red mud is such by-product in alumina production. Higher alumina production signifies higher production of bauxite residue, red mud. The worldwide alumina industry produces over 70 million dry metric tons of bauxite residue annually. This review paper is focused on patent literature for the purpose to give a summary of patents related to the topic of red mud treatment. It includes 88 patents from around the world filled between 1957 and 2002. Just few patents are in particular use with the sole objective of red mud treatment from alumna production. The explanation is the poor economic viability of red mud treatment in general. Most of recent patents combine several different methods to reach the objective of red mud treatment. It involves treatment of red mud from

alumina production by direct contact with solid, liquid or gas reactant and following hydrometallurgical, thermal or other kind of processing.

Keywords: Red Mud, Treatment, Bayer Process, Patents

Introduction

The extraction of alumina as alumina trihydrate from bauxite is accomplished by the well – known Bayer process. The main characteristic is the digestion of the bauxite in caustic liquor. However, bauxite contains impurities, which are insoluble in caustic liquor and create insoluble residue known as red mud. The production of one ton of aluminium metal yields 1.5 to 4 tons of a residue (on a dry basis) to be disposed. The worldwide alumina industry produces about 70 million dry metric tons of bauxite residue annually [1]. The red mud disposal could signify economical but also ecological problem. From the economics point of view it is potentially high life-cycle costs of future disposal, monitoring and uncertainty about total costs of residue disposal. From the ecological point of view it is production of large volumes of long-term, non-usable by-products, high alkalinity of mentioned by-product, potential for reclassification as a hazardous waste at some future time, potential of groundwater contamination, dusting during drying, higher than normal background radiation etc. These factors are the main reason of a big effort for treatment and recycling of valuable components from red mud.

Chemical and Mineralogical Composition of Red Mud

Red mud has a complex mineralization, which depends on the chemical and mineralogical composition of the processed bauxite and on the autoclaving conditions employed during the Bayer process treatment. It consists partly of minerals that do not dissolve during the caustic treatment of the bauxite and also of components originating during leaching (DSP). Red mud residue consists of minerals like hematite α–Fe_2O_3, goethite FeO(OH), boehmite $Al_2(OOH)_2$, gibbsite $Al(OH)_3$, anatase or rutile TiO_2, quartz SiO_2, calcium carbonate and calcium aluminates from lime addition, and also of what is known as the desilication product (DSP), which contains not only silica but also considerable quantities of unrecovered alumina and soda. Desilication product plays a critical role in the Bayer plant process since it provides the mechanism for the removal of silica taken into solution during digestion by caustic soda. Chemically this is hydrated sodium aluminium silicate, approximating to the natural mineral Cancrinite. A common chemical formula assigned to this material is $3Na_2O.\ 3Al_2O_3.\ 5SiO_2.\ 5H_2O.\ Na_2CO_3$. Universal agreement on a composition for this compound does not exist.

Chemical composition of red mud residue depends on chemical composition of bauxite and on the amount of materials added into the Bayer process. Typical bauxite residues contain 24-50% Fe_2O_3, 12-30% Al_2O_3, 5-17% SiO_2, 2-18% TiO_2, 0.5-6% CaO, 3-10% Na_2O. The residue also contains trace amounts of the metals gallium, zirconium, vanadium, thorium, scandium and rare-earth metals.

Possible Red Mud Utilization

Several methods are known for red mud utilization. This paper will focus on patent literature review. Patents issued between 1957 and 2002, from around the world were reviewed [2-88]. More than 88 patents were obtained, read and analysed. Number, date, author(s) and title

in table 1 classify the most pertinent patents during this period. They are presented in chronological order. The method, advantages and disadvantages described in each patent are also clearly summarised for potential readers.

The patents can be divided into several categories according to red mud utilization:

- Valorization: Recovery of sodium
  - Rare earth metals recovery
  - Oxides for ceramic industry
  - Metals, metal oxides, fluorides, chlorides
- Construction, building material
- Site restoration
- Pigment
- Steel production
- Other (PVC, plastic material etc.)

As is shown in Figure 1, the most of patents were focused on valorization of useful components contained in the red mud.

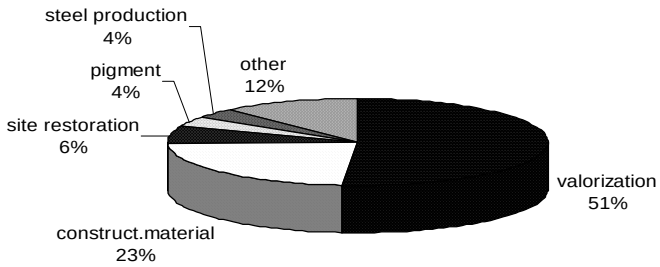

Fig.1 Proportion of patents according to red mud utilization

All the methods found in the patent literature can be summarized as follows:

- Hydrometallurgical
- Thermal + hydrometallurgical
- Thermo – mechanical
- Mechanical
- Thermal
- Other (ion–exchange, hydro–mechanical, magnetic separation, fluorination and chlorination, dissolving etc.)

The chosen method of red mud treatment depends on its physicochemical properties and also on fact if it's a complex utilization or an utilization focussed just on 1-2 components of red mud. Recovery of iron and steel has received the most significant attention in the past because of the dominant presence of iron oxide. Thermal methods like sintering, reduction smelting etc. has been widely examined. The main disadvantage of thermal methods is their big consumption of energy and economics would also require a low-cost technology for dewatering of the red mud. Processes aimed exclusively at utilization in iron metallurgy are economical only when high-content red muds are being processed.

The mechanical or thermo-mechanical methods have been used mainly for production of building materials and ceramics. Processes aimed at utilization for building materials may

significantly ease storage problems, but is none the less only partial solution. The main disadvantage of these low-cost methods is that final products (bricks, constructional blocks, building material) comprise components (sodium content, radionuclides), which can cause significant problems in the future. The radiation concern represents an unacceptable commercial risk to making building products from the residue. Hydrometallurgical and thermo-mechanical methods are preferred in patents issued between 1990 and 2002. The situation is probably due to present cost effective technologies with less consumption of energy and due to complex utilization with significant reduction of red mud amount. Other methods like ion–exchange, hydro–mechanical, magnetic separation, fluorination and chlorination, dissolving are some kind of alternative methods usually used in combination with previous above mentioned methods. The methods found in the patent literature are schematically summarized in Figure 2.

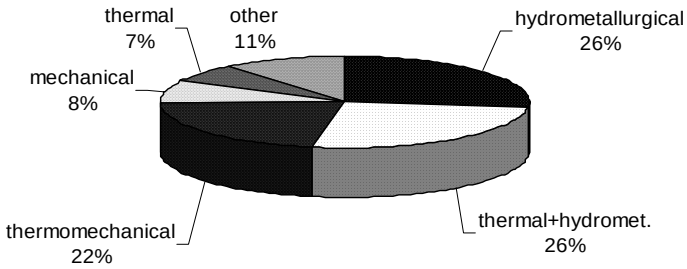

Fig.2 Methods of red mud treatment

Most of patents were issued between 1990 and 2002; some of them were refilled with upgrades. Improvements are often not very significant.

Some of the methods quoted above, to the author's knowledge, have been applied but all of them are still limited by economics (not cost effective technologies). No patent has seen worthwhile applications for the main purpose of red mud treatment. Proportion of patents according to time period shown in Figure 3 clearly demonstrates, that there is bigger effort to solve the problem of red mud residue in last decade.

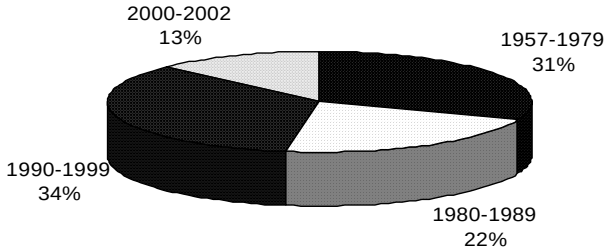

Fig.3 Proportion of patents according to time period

The following investigation has been made for purpose to find out countries, which have publicized patents about red mud treatment. Almost all of these countries produce alumina from bauxite ore and have large amounts of untreated red mud. Proportion of issued patents by country is shown in Figure 4.

- Asia (Japan, China, Taiwan, Korea, India)
- Hungary
- Germany
- Canada
- Australia
- USA
- Russia
- Other (France, Guyana, Guinea)

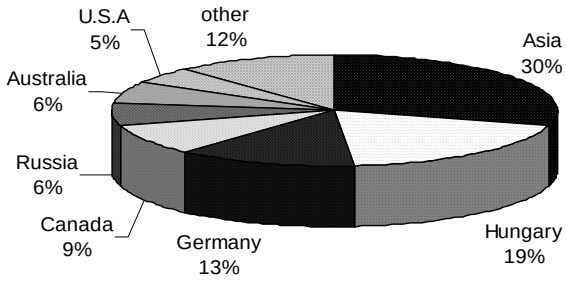

Fig.4 Proportion of issued patents by country

Conclusions

Most patents in use today were issued in the 80's. Some of these patents are in partial use with the objective of red mud treatment or utilization. This situation most likely results from absence of feasible economic solution to this problem. The disposal of above mentioned by-product could signify economical (high-cost dump maintenance), but also ecological problem (possible escape of hazardous substances to the environment). Upon prior research of many authors, the probable way in which to handle this problem is to combine different methods or combine treatment of suitable by-product mixtures, which would include red mud. To the authors of the recently written patent review, this appears as the most probable route to make red mud treatment process economically viable.

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