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P a r t 3

ASH AND SLAG HANDLING

3.5. Applications of ash and slag from power coals

3.5.6. Obtaining different substances from coal combustion by-products

3.5.6.2. Integrated recycling of ash and slag of Ekibastuz coals into aluminum oxide, aluminium salts, ferrosilicon and cement

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ABSTRACT

The paper contains the results of the designed alkaline and acidic methods of integrated recycling of power and self-disintegrated calcium aluminate slags, anorthite cakes and ash of low-temperature combustion of Ekibastuz coals with the output of end products. It shows the advisability of reorientation of the raw materials base of the Pavlodar aluminium plant from bauxites to self-disintegrated slags produced from ash slag of Ekibastuz coals, and of using released capacities of sintering process stage for the production of construction materials.

Steam thermoelectric power stations in Europe, USA, China and India are put into operation on a large scale owing to large coal reserves in the world and price stability for it. As predicted by the International Energy Agency, in the nearest decades, coal will retain its role in Europe and in the whole world [1, 2].

In the Republic of Kazakhstan, electric power is produced by 14 high-power thermoelectric power stations, where mainly Ekibastuz coals are fired. Further development of heat power engineering of Kazakhstan is based on the firing of Ekibastuz coals. Recently, the Senate of the RK Parliament ratified the Intergovernmental Agreement between Kazakhstan and the Republic of Korea *On Construction and Operation of Balkhash Thermoelectric Power Station*. Commissioning of block I of module I (660 megawatt) is planned in October 2017, and of the whole module I (1 320 megawatt), in April 2018.

The Law ratified is very important from the point of view of power safety of the Republic of Kazakhstan, since the construction of the power station ensures the required power reserve in southern Kazakhstan.

The coals of Ekibastuz basin, which reserves amount to over 11 billion tons, contain up to over 50 % of ash; over 15 million tons of ash is emitted at the operation of only two Ekibastuz state district power stations, and over 2 million tons will be emitted at the commissioning of the Balkhash power station. The ash of Ekibastuz coals contains SiO_2 (~50 %) and Al_2O_3 (~30 %). At that, it consists of chemically stable components in the forms of mullite and quartz. Such ash is highly abrasive that result in high abrasive wear of boiler heating surfaces. This ash is keroid that causes poor trapping in wet Venturi scrubbers; besides, it is high-resistant that leads to inefficiency of electric filters. The consequence of all this is the atmospheric pollution of untrapped silicon dioxide ash. Due to the lack of binding components in the ash, no solid crust is formed at ash dumps, and dust is raised in the wind, thus causing secondary environmental pollution with already trapped ash. At the same time, a mineral part of fuel contains such valuable components as aluminum, iron and other metals as well as rare earth elements, rare and dispersed elements, for the production, delivery and refining of which much funds are spent in the metallurgical industry [3, 4].

During several years the Kazakh National Technical University after K.I. Satpayev has been developing scientific basics and technologies of integrated recycling of aluminum-containing ash slag of Ekibastuz coals, which can be a source of aluminum salts, aluminum oxide, ferrosilicon, rare metals and other products for the economy [5].

The studies conducted with regard to the creation of scientific basics and technologies of alkaline and acidic methods ensured the proposal of new technical solutions and methods of integrated recycling of alkali-free aluminum-containing raw materials. Cost effectiveness of these methods was determined by means of comparing of the existing or already applied technologies. At that, results of research works and semi-commercial tests as well as the actual data of operation of non-ferrous and chemical companies have been used.

Alkaline method of recycling of self-disintegrated slag. Integrated recycling of the mineral part of Ekibastuz coals with the production of heat energy, aluminum oxide, ferrosilicon and cement, proposed and developed by us, ensures the use of ash slag wastes for the production of artificial raw material directly at the fuel combustion and the considerable solution of environmental issues [6].

Power technical complex on the basis of Ekibastuz coals includes the following main process stages:

- Combustion of coal fluxed with limestone or dumping sludge from the Pavlodar Aluminum Plant (at the rate of 10-12 % of coal weight) in cyclone furnaces with slag drip;
- Lime reclaiming into liquid energy slag and smelting of furnace charge in the heated accumulating tank (Certificate of authorship №1108033).

Combination of a cyclone furnace with an electric accumulating furnace (Certificate of authorship № 1203346) will ensure considerable reduction of power costs for the smelting of self-disintegrated calcium aluminate slag and ferrosilicon (Certificate of authorship № 1274346) due to the use of liquid slag heat. Since 1-2 % coal of the weight of the mineral part is needed for complete reduction of iron oxides and a part of aluminum oxide, the reduction processes can be realized due to an unburned part of coal and CO. After the cooling and dispersal, the material is exposed to the screening stage. 1-3 mm fraction consists of ferrosilicon. Calcium aluminate slag the size of which is less than 1-3 mm is sent to soda leaching with subsequent division of aluminate mud and sludge (№ 1365617 and 1434703). The aluminate mud is processed into aluminum oxide using a known technology, and a sludge with low content of iron oxides (less than 0.1 %) and sodium (less than 1 %) and high content of CaO (57-64 %) and SiO_2 (24-30 %) is a quality raw material for the production of white and colored cements. Combined firing of Ekibastuz and Kansko-Achin coals with 60 % content of CaO in the mineral part and 8-12 % of Al_2O_3 is possible. In this case, self-disintegrated calcium aluminate slag can be produced without thermal-electric process stage directly in a cyclone furnace with slag drip. At the mixing of brown coals their disposition to spontaneous ignition is reduced; and at their firing, excessive calcium oxide is bound into aluminates and calcium silicates that eliminates the formation of calcium sediments on the heat-exchange surface. It is proposed to fire Ekibastuz coals fluxed with lime in cyclone furnaces with slag drip and to bring the liquid melt to the optimal composition by means of lime reclaiming to the heated accumulated tank. This will ensure a 30-40 % decrease of aluminum oxide cost as well as the avoidance of the need in separate construction of power-intensive units – rotary sintering furnaces that will result in the saving of material and human resources. In addition, hydrometallurgy process stages can be implemented at alumina plants without any changes in their equipment flowcharts.

Feasibility study of the method done by the All-Union Aluminum-Magnesium Institute (AUAMI) proved its efficiency. Comparison was done using AUAMI's methods – sintering of the overburden of Ekibastuz coals in rotary furnaces with lime and producing self-disintegrated cakes. Using the developed method, the annual economic effect of the aluminum oxide production (without ferrosilicon cost) using the mineral part of Ekibastuz coals will amount to 3.08 million rubles (in prices of the year 1988) at the production rate of aluminum oxide of 500 thousand tons compared to the AUAMI's method of lime sintering and it will be significantly higher in case of ferrosilicon sale. The economic effect of the implementation of the recycling method of the mineral part of Kansko-Achin (Berezovskiy coalfield) coals will amount to 7.5 million rubles a year at the firing of 50 million tons of coal with the production of 4 million tons of slag, 400 million tons of ferrosilicon at the plant's production rate of 500 million tons of aluminum oxide and 5 million tons of cement.

Acidic technologies of integrated recycling of ash slag of Ekibastuz coals. Sulfuric acid method resulting in the production of aluminum sulfate (coagulant), aluminum oxide and binders was proposed and developed for the purpose of recycling of the energy slag of the ash produced as a result of low-temperature combustion of Ekibastuz coals [7].

On the basis of a complex of studies and development works, a process flowchart of aluminum sulfate and aluminum oxide production from energy slag of Ekibastuz coals was developed; it consists of the following main operations:

- Combustion of Ekibastuz coal fluxed with limestone with the production of granulated energy slag (Certificate of authorship №488787);
- Sulfuric acid leaching of grinded energy slag and division of suspension along with the sludge washing;
- Recycling of product solutions into aluminum sulfate and aluminum oxide;
- Regeneration of sulfuric acid.

In harmony with semi-commercial tests, LENNIIGIPROKHIM has developed a feasibility study and selected primary and auxiliary equipment, prepared drawings for its assembling and calculated capital costs. At the replacement of the existing technology of aluminum sulfate production using aluminum hydroxide with the developed method of its production using energy slag of Ekibastuz coals (standard workshop 150 thousand tons), major economic effect will amount to 300 thousand rubles.

At the sulfuric acid recycling of the low-temperature combustion ash (Certificate of authorship № 694453, 908747) it is grinded till the size of 2.5 mm. Low-temperature combustion ash is leached with 18 % H_2SO_4 at the temperature of 95-100 ^{0}C during 1.5 hours, the product suspension is divided in a vacuum filter with two-stage washing of the sediment. The product solution, containing 5 % Al_2O_3, is exposed to concentration in vacuum evaporators till the concentration of 15 %. Crystallization of evaporated solution is done in the course of cooling on belt conveyers resulting in solid coagulant in the form of 15-mm thick plates.

To treat sulfuric acid solutions from iron it is possible to apply ampholyte ANKF-3G or cationite KM-2P. Macroporous cationite KM-2P is the most perspective with regard to the use since it is characterized with high capacity for iron and exclusive selectivity, possesses thermal stability and is available from the producers.

Si-stoff can be used as a component of raw mix in the production of cement clinker using a dry method (Certificate of authorship №937390). In compliance with the data of GIPROTCEMENT, the expected economic effect of the replacement of bauxite sludge with si-stoff will amount to 136 thousand rubles at the plant capacity of 630 thousand tons of cement per year.

LENNIIGIPROKHIM has done a feasibility study of the method that revealed that profitability and payback period are commensurable with the values accepted in the chemical industry.

In 1980ies, a fluidized bed boiler, created on the basis of an off-the-shelf boiler DKVR-25-14 of the Biysk boiler plant, was commissioned in the city of Zhezkazgan. It is possible to organize the sulfate production at the Zhezkazgan ore mining and processing enterprise where there is abundance of sulfuric acid as a byproduct of the main production. Low-temperature combustion ash disposed at the dump is sufficient for the aluminum sulfate production; the effect will amount to 725 thousand rubles a year.

Nitric acid method resulting in the production of aluminum oxide, nitrate fertilizers and si-stoff was proposed and developed for the recycling of anorthite cakes and energy slag of Ekibastuz coals. The anorthite cake can be recycled in two options (Certificate of authorship № 1194841): it is treated with 18 %-nitric acid dosed only for CaO at the temperature of 240 ^{0}C. At that, HNO_3 reacts with CaO and forms calcium nitrate; the pulp is filtrated and CO_3 is precipitated from the calcium nitrate solution by means of carbonization $(NH_4)_2CO_3$. Upon the separation from calcium carbonate, NH_4NO_3 solution is supplied for the production of ammonium fertilizers. Alumina residue is exposed to 30-35 % HNO_3 leaching. The pulp obtained is filtered and aluminum hydroxide is extracted from nitric acid solution using hydrolysis.

In compliance with option 2, the anorthite cake is delivered for nitric acid (30-35 % HNO_3) leaching; at that, the acid is dosed for the formation of aluminum and calcium nitrates. Conditions chosen ensure selective transfer of Al_2O_3 (up to 88-92 %) and CaO (up to 88 %) into the solution, precipitating iron compounds. The product nitrate solution contains 60-73 g/dm^3 of Al_2O_3 and 51-60 g/dm^3 of CaO. After the filtration, the nitrate solution is evaporated. Si-stoff is exposed to the two-stage washing at liquid to solid ratio of 2.5:1; its output amounts to 2.5 t per 1 ton of aluminum oxide. With the purpose of selective decomposition of calcium and aluminum nitrates, after crystallization a nitrate fusion cake is exposed to thermal treatment at 400 ^{0}C during 25-30 minutes. The obtained product is treated with water at 60-80 ^{0}C at liquid to solid ratio of 3:1 in agitation conditions. At that, $Ca(NO_3)_2$ transforms into water solution and aluminum compounds remain in solid residue. After the filtration, the alumina residue is recycled into crude Al_2O_3, and nitrate solution, into fertilizers.

It is more efficiently to recycle energy slag using nitric acid method resulting in alkaline product for the production of metallurgical aluminum oxide (Certificate of authorship. № 976610). Granulated energy slag is grinded and exposed to agitation leaching using 35-40 % nitric acid at the temperature of 90 ^{0}C during 60 minutes. At that, aluminum oxide extracted into the solution amounts to 90-95 %. For the filtration, vinyl chloride tissue possessing sufficient chemical stability, mechanical strength is used that ensures its use at the temperature of 80-90 ^{0}C. The output of siliceous sludge is 2.57 t per 1 ton of alumina and can be used for the production of binding materials, Portland cement, container glass and adsorbent for oil products. Nitrates solution is exposed to vaporization at 135-145 ^{0}C and decomposition in a tube furnace at 750-850 ^{0}C. Acid regeneration at the decomposition of a fusion cake of nitrate salts is done by means of its condensation from exhaust gases using a method widely applied at chemical plants for the production of nitric acid. Aluminate cakes are leached using soda-alkaline solutions resulting in aluminate solutions, g/dm^3: 120-150 Al_2O_3; 115.6-128.4 Na_2O; 0.03 Fe_2O_3; 0.1 SiO_2, which are then recycled to aluminum oxide by means of a known technology. The feasibility study of the combined method carried out by AUAMI demonstrated rather high cost-effectiveness of the developed technology. In conformity with the proposed technology, the costs per 1 ton of aluminum oxide comply with the AUAMI's design data for perspective plants (Severoonezhskiy and others), and a pay-back period of capital investments is 6.3 years.

Hydrochloric acid method was proposed and developed for the recycling of ash of Ekibastuz coals into alumina oxide and byproducts. Low-temperature combustion ash is leached at the temperature of 100-105 ^{0}C during 2.5 hours in 20 % hydrochloric acid (consumption of acid is 105 % of stoichiometric ratio). Filtration (Certificate of authorship №1397410) of hydrochloric acid pulps is done using vacuum filters at 25 ^{0}C; for the avoidance of acid loss, 0.2 % polyethylene oxide solution or 0.5 % A-1 is added at the relevant consumption of pulp at the rate of 0.02 and 0.08 kg/m^3 of the pulp. The flushing is done with hot water (70-80 ^{0}C) at liquid to solid ratio of 1.5:1 in three stages. Vaporization of solutions is done at 110 ^{0}C. Thermal decomposition of chlorides (Certificate of authorship №1258815) is realized in the presence of water vapors at 140 ^{0}C during 1 hour with the consumption rate of crude aluminum oxide 5.5 t/t which is exposed to water flushing at 25 ^{0}C at liquid to solid ratio of 3:1 during 0.5 hour. The flushed crude aluminum oxide is recycled according to the simplified Bayer's process. After the filtration and flushing, si-stoff is formed which is supplied for the production of construction materials (additive to Portland cements, glass production etc.). Red mud containing up to 63 % of iron, 0.26-0.65 % of vanadium, 4.8-5.8 % of titanium, is supplied for the production of cast iron, vanadium slag or titanium. The feasibility study done by the Institute of Economy of the Academy of Sciences of KazSSR revealed that profitability of the technology is 19-21 %, the pay-back period is nearly 5 years.

Thus, developed alkaline and acid methods of integrated recycling of energy and self-disintegrated calcium aluminate slags, anorthite cakes and ash of low-temperature combustion of Ekibastuz coals are quite perspective for their industrial implementation. On the basis of the studies, development and design works conducted by us, the USSR Ministry of Energy made a decision regarding the organization of production of energy and self-disintegrated slag of Ekibastuz coals and its commissioning at the rated capacity in the year 1995.

The results of the studies conducted were used at the designing of the preassembled integrated plant at the Almalyk chemical plant for the recycling of aluminum-containing raw material using acid methods as well as at the LENNIIGIPROKHIM designing of coagulant production master plan in the USSR.

The USSR Ministry of Non-Ferrous Metallurgy made a decision regarding the replacement of scarce aluminum hydroxide with the aluminum oxide production wastes and ash slag of Ekibastuz coals for the production of aluminum sulfate.

In view of triple delayed rates of development of aluminum oxide production and its raw materials base compared to the rates planned within the major directions of economic and social development of the USSR national economy for the XII five-year period and the year 2000 as well as in view of the need to improve the environmental situation in the region of Ekibastuz Fuel and Energy Complex, the Kazakh SSR Council of Ministers submitted to the USSR State Planning Committee a proposal regarding the creation of the Ekibastuz alumina and aluminum complex based on the technologies developed by the author.

At the initial stage of implementation of this proposal, with the purpose of significant reduction of capital investments it was advisable to change the orientation of the raw materials base of the Pavlodar Aluminum Plant and Achin Aluminum Oxide Complex from bauxites and nephelines to self-disintegrated slag produced out of ash slag of Ekibastuz and Kansko-Achin coals, and to use the freed capacities of the sintering process stage for the production of construction materials.

In 1988, the USSR Ministry of Energy jointly with the USSR State Committee of the Council of Ministers for Science and Engineering held a competition for environmentally clean power station on solid fuel. The work proposed by the author along with the number of the institutes and companies of the USSR Ministry of Energy won the competition and was included in the State Scientific and Engineering Program "Environmentally Clean Power Engineering".

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