ANNOTATION

Dissertations for the degree of Doctor of Philosophy (PhD) in the specialty 6D070900 – «Metallurgy»

BAKIROV ALTYNSARY GAZIZOVICH

RESEARCH AND DEVELOPMENT OF TECHNOLOGY FOR THE EXTRACTION OF ALUMINA AND USEFUL COMPONENTS FROM ASH AND SLAG WASTE USING PRE-ACTIVATION

The relevance of the topic of the dissertation work. Ash and slag waste from thermal power plants of the fuel and energy complex can serve as a possible source of extraction of useful components and alumina. Ash and slag waste, contain 25-30% Al_2O_3, 5-7% Fe_2O_3, 50-60% SiO_2, 0.2–0.7% Na_2O, 0.7–1.5% TiO_2, 0.010%, V_2O_5, 36 g/t gallium, underburning 6-14%. For Kazakhstan and the whole world, the involvement in the processing of non-traditional sources of alumina-containing raw materials, including (ZCO) is relevant. According to geological data, the reserves of bauxite deposits in Kazakhstan are calculated for 50-60 years. Turgay bauxite mine has ceased to function as a deposit. Technological changes in bauxite processing are becoming more complicated every year, this is due to an increase in more impurities in the initial bauxites, such as organic impurities, chlorites, carbonates, sulfates). These factors have a negative impact on technological indicators and processing of alumina production. This proposed technology will create an alternative to the production of alumina from nephelins by the sintering method. The development of an effective waste-free technology for processing ash and slag waste from thermal power plants with the extraction of alumina and useful components is very relevant.

The purpose of the dissertation is to research and develop a technology for extracting alumina and useful components from ash and slag waste using pre-activation.

Scientific novelty of the results obtained: - for the first time, new data on the thermodynamics of reactions of the interaction of ash and slag waste components with NaHCO3 during chemical activation in the temperature range of 60-200 ° C. The possibility of decomposition of mullite, sillimanite, bound silica with the formation of amorphous phases of mullite, free silica is shown. - for the first time, a method of flotation enrichment using pre-activated ash and slag waste has been developed, including the separation of carbon concentrate and aluminosilicate microspheres, which made it possible to extract carbon concentrate with a carbon content of 65% using kerosene and methyl isobutyl carbinol reagents; - it was determined that during chemical activation, changes occur in the mullite towards a decrease in the silica content in it, the content of free silica increases from 8.7 to 36.1% and the calcite phase ($CaCO_3$) is formed. It is established that the optimal temperature of chemical activation is 150 ° C, a further increase in temperature

leads to minor changes in the phase composition. For the first time, the possibility of extracting alkali-soluble forms of ash and slag waste using chemical activation in a solution of sodium bicarbonate with a content of 120 g/dm3 has been studied. The use of pre-activated ash and slag waste showed an increase in silica extraction at almost all temperature parameters and NaOH concentration. At a NaOH concentration of 100 g/l (120 °C), silica extraction under normal conditions reached 52.1%. The use of pre-activated ash and slag waste in similar conditions increased the extraction of silica to 68.3%. - It was found that after the use of pre-activated ash and slag waste, the desilination process is intensified with a decrease in duration from 300 min to 120 min.; Kinetic features of reactions are investigated for the first time

$$SiO_2+2NaOH+H_2O=Na_2SiO_3+2H_2O \quad (1)$$

$$3Al_2O_3\cdot 2SiO_2+4NaOH+H_2O=2Na_2SiO_3+3Al_2O_3+3H_2O \quad (2)$$

$$Al_2SiO_5(S)+2NaOH+H_2O=Na_2SiO_3+Al_2O_3+2H_2O \quad (3)$$

interactions of free and bound silica with sodium hydroxide (NaOH) during desilinization of ZCO. - it was determined that during desilinization of ash and slag waste, the activation energy was 38.1 kJ/mol, under the same conditions with the use of pre-activated ash and slag waste, the activation energy was 33.5 kJ/mol. The possibility of sintering ash and slag waste in three-component charge systems with the production of self-disintegrating sinters is investigated. - it was found that the optimal sintering temperature of ash and slag waste is 1200 ° C with a duration of 60 minutes, the extraction of alumina (Al_2O_3) was – 90.2 %; - it has been established that in this area $2CaO\cdot SiO_2$–$12CaO\cdot 7Al_2O_3$–$CaO\cdot Al_2O_3$ the main alumina-containing phases are $CaO\cdot Al_2O_3$ and $12CaO\cdot 7Al_2O_3$, which are highly soluble in soda-alkaline solutions when leaching alumocalcium sinters at a temperature of 70 ° C.

By the method of probabilistic deterministic planning of the experiment, partial dependences of the desilinization process of ash and slag waste with NaOH were obtained, which establishes the effect of duration and temperature on the degree of transition of silica into solution, and the desilinization process was optimized. The novelty of the research results is also confirmed by the patent for the utility model of the Republic of Kazakhstan No. 7243 dated 01.07.2022 "Method for processing ash and slag waste of thermal power plants". A method for processing ash and slag waste from thermal power plants, including the release of carbon concentrate (unburned carbon) and aluminosilicate products (microspheres), characterized in that before the release of unburned carbon from ash and slag waste, a chemical activation operation is performed by treating a solution containing 120 g / dm3 sodium bicarbonate, at a temperature of 150 ° C for 60 minutes in an autoclave.

The main provisions submitted for protection - new data on thermodynamic analysis of reactions of interaction of ash and slag waste components with sodium bicarbonate; - results of flotation enrichment of pre-activated ash and slag waste; - results of the study of the kinetics and mechanism of desilinization of pre-activated ash and slag waste with an alkaline solution (NaOH); - results of laboratory studies of sintering of ash and slag waste on three component charge systems; - results of enlarged laboratory tests of hydrometallurgical and pyrometallurgical processing of ash and slag waste. Practical significance of the work.

The results of research and testing will be used in the energy and metallurgy industries with the development of technological regulations on the basis of which a technical and economic assessment of the construction of an alumina plant from ash and slag waste of thermal power plants in the Pavlodar region will be issued.

Publications and approbation of the work. According to the results of the dissertation, four articles were published, including:

one article in a journal included in the Scopus database (Q3, 38th percentile);

- Bakirov A.G., Abdulina S.A., Zhunusov A.K., Oleinikova N.V., 2021, Preliminary chemical activation of ash waste with release of carbon concentrate, Chemical Engineering Transactions, 88, P. 973–978. DOI: 10.3303/CET2188162.

- three articles in journals recommended by the Committee for Control in the Field of Higher Education and Science of the Ministry of Higher Education and Science of the Republic of Kazakhstan.

- Бакиров А.Г. Абдулина С.А., Жунусов А.К.(2019) «Исследование химико-минералогического состава золошлаковых отходов Аксуской энергетической компании». «Вестник ВКГТУ» № 2, С. 25–29

- Бакиров А.Г., Жунусов А.К., Абдулина С.А., Ибраева Г.М. (2020) Исследование алюмосиликатных микросфер из золошлаковых отходов Аксуской ГРЭС, использующей Экибастузские угли «Вестник ВКТУ» № 4, С.72–77

- Бакиров А.Г., Жунусов А.К., Абдулина С.А., Буленбаев М.Ж. (2022) Технология переработки золошлаковых отходов ТЭС способом спекания. «Труды университета» Караганда, КарТУ, № 4, С. 103–107.

- a patent was obtained for a utility model of the Republic of Kazakhstan «A method for processing ash and slag waste from thermal power plants».

The main provisions and results of the work were tested at three international conferences in the form of oral reports:

- Бакиров А.Г. Абдулина С.А., Жунусов А.К., Олейникова Н.В. (2019) «Анализ образования золошлаковых отходов и переработка их различными способами» Материалы научно - практической конференции посвященной 120-летию К.И. Сатпаева. С. 186 –189;

- Бакиров А.Г. Абдулина С.А., Жунусов А.К., Олейникова Н.В. (2019) «Комплексная переработка золошлаковых отходов ГРЭС» Сборник докладов одиннадцатого международного конгресса «Цветные металлы и минералы» - Красноярск (РФ), С. 1014–1018.

- Altynsary Bakirov. 24 th Conference on Process Integration, Modelling and Optimisation for Energy Saving and Pollution Reduction. PRES’21.0037

Preliminary chemical activation of ash and slag waste with the release of carbon concentrate. 31st October to 3 rd November 2021, in Brno, Czech Republic (Online)

The structure and scope of the dissertation. The dissertation consists of an introduction, five chapters, a conclusion and seven appendices. The work is presented on 151 pages of typewritten text, contains 57 tables, 76 figures. The list of sources used includes 140 titles.