ANNOTATION

dissertation work topic:

"DEVELOPMENT OF COMPLEX TECHNOLOGY OF ASH PROCESSING WITH EXTRACTION OF VALUABLE METALS",

presented for the degree of Doctor of Philosophy (PhD)

on a speciality 8D07204 - "Metallurgical engineering"

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The aim of this dissertation work is to create an innovative environmentally friendly, highly efficient, waste-free technology for ash utilization with obtaining marketable products using low-cost methods of chlorination sintering, leaching, aluminum chloride crystallization from the solution and low-temperature sintering.

Research objectives:

- Based on the analytical review, the current state and prospects of development of the coal industry, the choice of research direction.
- Study of theoretical features of chloride sintering processes of ash. The data obtained were used to carry out laboratory research of calcium chloride ash roasting process of Almaty TPP.
- Study of the process of leaching pre-burned ashes with hydrochloric acid.
- Study of the theoretical foundations and experimental justification of the extraction of alumina from aluminum-containing hydrochloric acid solutions.
- Development of a general technological scheme for the complex processing of ash and obtaining commercial products.
- Technical and economic evaluation of ash processing technology.

Research Methods. The basic methods of researches and the analyses used at performance of dissertational work, include: a complex of modern physical and chemical methods of the analysis of raw materials and products of its hydrometallurgical processing: Atomic absorption analysis (PinAAcle spectrometer by PerkinElmer), optical emission analysis (inductively coupled plasma spectrometer by Agilent 710 ES), thermogravimetric analysis (analyzer by Mettler Toledo), X-ray phase analysis (X'Pert PRO X-ray diffractometer by PANalytical), structural analysis (scanning electron microscope JSM-6390LV by JEOL Ltd. "), infrared spectroscopic analysis (FT-801 infrared spectrometer by Simex);

Main provisions (proven scientific hypotheses and other conclusions which are new knowledge) defended:

- results of thermodynamic calculations of Gibbs free energy of reactions of interaction of ash components with $CaCl_2$ in oxidizing atmosphere in the temperature range 900-1100 °C.

- New data on thermodynamics and kinetics of cinder leaching process by hydrochloric acid, optimum leaching parameters allowing maximum separation of silica in commodity product and more than 99% of aluminum in solution.

- New data on the mechanism of thermal decomposition of ACH and optimal parameters of the thermal decomposition process of ACH.

- optimum parameters and modes of a complex technology of ash processing, including the results of each individual process, constituting the general concept of the technology.

- The developed technological scheme of complex ash processing with obtaining marketable products - iron product, pure silica and alumina, applicable to the processing of accumulated and current ash and slag waste of TPPs in Almaty.

Description of the main results of the study.

- New data on thermodynamics of reactions of interaction of ash components with calcium chloride were obtained. A high probability of mullite decomposition by calcium chloride in an oxidizing atmosphere by reaction (11) to helenite ($Ca_2Al_2SiO_7$) was established. The free Gibbs energy of reaction (11) increases sharply from $\Delta G1073K$ = -1226.0 kJ/mol×K to $\Delta G1373K$ = -2317.57 with increasing temperature from 1073 to 1373 K. Gehlenite formation increases in the presence of water (reaction 12), as evidenced by high Gibbs free energy values, which at 1073 and 1373 K are: $\Delta G1073K$ = -1309.74 kJ/mol×K and $\Delta G1373K$ = -2524.42 kJ/mol×K.

- New data for thermodynamics and kinetics of cinder leaching with hydrochloric acid were obtained. The mechanism of the leaching process described by the reaction of anorthite and gehlenite interaction with HCl with formation of $AlCl_3$ with its further transfer to the mother liquor has been established. It has been found that the reaction rate of interaction of anorthite and helenite with HCl increases at a temperature of 60 ºC and S:L=1:3.

- It was experimentally proved that it is possible to extract up to 80% of iron from ash by means of magnetic separation into a commodity iron-containing product with a high iron content ~50%. A material balance of the process was compiled, elemental and phase composition of the magnetic and non-magnetic ash fraction was determined.

- Optimal parameters of sintering of non-magnetic ash fraction together with calcium chloride in oxidizing atmosphere were determined: temperature - 1100 ºC, $CaCl_2$ consumption - 2 times higher than its stoichiometric consumption necessary for mullite decomposition, roasting duration, τ=60 min. The maximum mullite decomposition to gehlenite and anorthite over 98 % has been achieved.

- New data on the leaching of cinder with hydrochloric acid with selective transfer of aluminum, calcium, iron, nonferrous metals and REM into the mother liquor and separation of silica as a commercial product have been obtained. Optimal parameters of the leaching process were determined: S:L=1:3, temperature, T=60 °C, leaching time, τ=60 min. The maximum extraction of aluminum in the solution and of silica in the commercial product - 99.92 and 99.8 %, respectively - was achieved under optimal roasting conditions.

- As a result of heat and power plant ashes processing according to the scheme: magnetic separation - sintering of non-magnetic fraction of ash together with $CaCl_2$ - carbonate leaching with hydrochloric acid, commercial product containing iron and pure silica was received, mass %: 99,5 SiO_2; 0,02 Al; 0,07 Ca; 0,02 Fe. The sediment whiteness is 92%, specific surface area (SFA) is 165 m^2/g, oil saturation (linseed oil) is 140 g/100 g.

- The laboratory crystallizer is developed and optimum parameters of crystallization process are stated: T=60 ºC, HCl concentration in a solution - 26-30 %, HCl-gas consumption - 0.5 l/min, duration - 1 h to provide high to 95 % extraction of aluminum from a solution in a form of $AlCl_3$-$6H_2O$ crystals.

- For the first time, laboratory setups for investigation of the thermal decomposition of $AlCl_3$-$6H_2O$ crystals by three independent methods: in the static state, in the suspended state and in the fluidized bed. It was found that the maximum decomposition of $AlCl_3$-$6H_2O$ to Al_2O_3 is achieved at 400 ºC. Increasing the temperature to 500 °C reduces the residual chlorine content in the alumina to 0.71 %.

- For the first time the mechanism of thermal decomposition of ACH and the temperature range of water and Cl-ions removal in the form of hydrogen chloride (235-250 ºC) from aluminum chloride hexahydrate have been determined.

- For the first time the optimum parameters of the thermal decomposition of HCA were determined: T = 400 ºC and duration, τ = 1 hour. The obtained aluminum oxide corresponds to grade G-00 according to GOST 30558-98 "Metallurgical Alumina" and can be used as a raw material for aluminum electrolysis.

- For the first time new data on the rectification of mother liquors were obtained. The possibility of extraction of non-ferrous metals and REMs in the form of cake (sediment) from the mother liquor by 25 % NH_4OH solution has been experimentally proved. It is established that the treatment of the solution with

ammonium hydroxide achieves high to 99.9% extraction of non-ferrous metals and REM in the intermediate product, suitable for further processing by known metallurgical methods. The optimum technological parameters of the rectification process have been determined: NH_4OH consumption by 20% more from its stoichiometric amount required according to reaction (8); temperature - 293 K; the duration of the process - 90 min.

- The technological scheme of complex ash recycling was developed to produce marketable products: an iron-containing product with high iron content up to 50 %, pure silica with 99.9 % SiO_2 content, and metallurgical alumina of G-00 grade suitable for aluminum production.

Substantiation of novelty and importance of the obtained results.

In Kazakhstan, the annual output of ash and slag waste is about 19 million tons. To date, more than 300 million tons of waste has been accumulated in ash dumps. In Almaty, a major megalopolis in Kazakhstan alone, more than 2 million tons of ash and slag wastes have been accumulated as a result of TPP-1, TPP-2 and TPP-3. In one heating season alone, about 600 thousand tons of ash waste is added to the accumulated volumes of ash from coal combustion. In the South Kazakhstan region, as a result of the Kentau TPP, a number of ash dumps have been formed, which have taken vast areas out of land use and have a negative impact on the environment (pollution of soil, air, groundwater).

The integrated technology of ash processing developed in the work will solve a number of important issues:

1.Utilization of ash from TPPs, especially those located within the boundaries of large cities, will significantly improve the ecological situation.

2. extraction of valuable components will provide an additional added value in the use of coal.

Compliance with the directions of development of science or state programs.

The results of the research presented in this dissertation are closely related to the research project implemented under the state grants of the Science Foundation of the RK: № AP09259637 "Development of high efficiency non-waste technology for utilization of ash from coal combustion with obtaining marketable products" for 2021-2023.

Description of the PhD student's contribution to the preparation of each publication.

The author's personal contribution consists in setting the goal and objectives of the work, conducting research, processing and analyzing the results, formulating conclusions, writing articles and abstracts.

On the topic of the dissertation work 11 scientific papers were published, including: 1 article in scientific journals included in the Web of Science database; 2 articles in scientific journals included in the Scopus database; 4 articles in scientific journals recommended by CCES MES RK.

The main results of the dissertation work were presented and discussed at the International Scientific and Practical Conferences:

1. Zholdasbay E. E., Kurmanseitov M. B., Daruyesh G. S., Argyn A. A., Dosmukhamedov N. K. To a complex technology of ash processing: Thermodynamics of chloride roasting. Modern Scientific research: Achievements, Innovations and Development prospects. Proceedings of III International scientific and practical Conference. Berlin, Germany, August 29-31, 2021. P.94-102.

2. Zholdasbay E. E., Kurmanseitov M. B., Daruyesh G. S., Argyn A. A., Dosmukhamedov N. K., Egizekov M. G. The concept of complex ash processing technology based on chlorination firing. International Scientific innovations in human life. Proceedings of II International Scientific and Practical Conference. Manchester, United Kingdom, 25-27 August, 2021. P. 130-137.

3. Kaplan Valery, Dosmukhamedov Nurlan, Zholdasbay Erzhan, Daruyesh Galamat, Argyn Aidar. Alumina and Silica Produced by Chlorination of Power Plant Fly Ash Treatment. WOCA (World of Coal Ash), 2022. Northern Kentucky Convention center Covington, Kentucky, May 16-19, 2022.

Dosmukhamedov N.K., Kaplan V.A., Zholdasbay E.E., Daruyesh G.S., Argyn A.A. Removal of Iron-content Magnetic Fraction from Fly Ash after Ecibastuz Coal Burning. WOCA (World of Coal Ash), 2022. Northern Kentucky Convention center Covington, Kentucky, May 16-19, 2022.