Conference Paper

Features of Waste Chemical Processing Germanium Concentrates

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Abstract

In order to increase the extraction of germanium in the technology of production of germanium concentrates, as well as finding ways to eliminate the accumulation of toxic waste using modern techniques and equipment, the physical and chemical properties of waste chemical processing of germanium concentrates (OHGC) of two domestic enterprises were experimentally studied. The main components of OHGC are: sulphate hemihydrate $CaSO_4{\cdot}0.5H_2O$ and hypochlorite $Ca(OCl)_2$ calcium. The moisture content of the sludge amounted to 30–50 %. The content of germanium in the cakes of both companies is in the range of 0.20 and 0.27 %, respectively, indicating the feasibility of recovery in the Ge. At the same time, the samples of cakes differ significantly in the content of impurities, which depends on the types of raw materials in the preparation of concentrates. Granulometric composition of cakes is characterized by high dispersion. With an average diameter of 12 μm, all particle sizes are in the range of 0.5-15 μm. The distribution of particle sizes is shifted in interval of 0–15 μm, and the area of the particles less than 3 μm is not more than 10 %. The high dispersion of the cake is reflected in the specific surface area, which is 23.7 m^2/g. Thermographic study found that the heating of the sample cake is accompanied by two endothermic effects of dehydration at 110 and 145–168 °C calcium sulfate and hypochloride semihydrate with corresponding weight loss of 13.1 and 12.9 %. The presence of toxic impurities (arsenic, zinc and lead), as well as chlorine, presents significant challenges for the development of disposal technology with the extraction of germanium. Assuming that the undiscovered part of the germanium in the concentrate is compounds or solid solutions with silicon dioxide, an effective technology should include their reagent high temperature treatment.

Keywords: waste, germanium concentrate, chemical processing, waste, physical and chemical properties.

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Published: 31 December 2020

Publishing services provided by Knowledge E

Selection and Peer-review under the responsibility of the TECHNOGEN-2019 Conference Committee.

1. Introduktion

In Russia, after the collapse of the USSR from 1994 to 2001, the production of germanium from proprietary raw materials did not exist. Since 2001, Russia has managed to partially restore its own raw material base. After the restructuring remain non-traditional mineral raw material base for production of germanium. While in the world germanium is mined simultaneously during the processing of lead-in-zinc ores, in Russia all industrial

How to cite this article: Igor Nikolaevich Tanutrov and Marina Nikolaevna Sviridova, (2020), "Features of Waste Chemical Processing Germanium Concentrates" in *IV Congress "Fundamental research and applied developing of recycling and utilization processes of technogenic formations"*, KnE Materials Science, pages 359–367. DOI 10.18502/kms.v6i1.8110

reserves of germanium are concentrated in lignit and coal deposits. The highest degree of enrichment during the processing of germanium-containing lignit and coal (20–30 times) is achieved by layer combustion. In this case, the bulk of the mineral component of raw remains in the slag, and germanium passes into the gas phase and is captured during coarse and fine cleaning in the form of fly ash.

After the resumption made of germanium from domestic raw materials, the technology of recovery melting with the participation of IMET UB RAS [1]. The raw materials used products layer combustion: coarse and fine dust, and slag. A product of the process are germanium-containing sublimates, organized bathrooms in the result of melting of a specially prepared mixture. Before melting, the charge formed during grinding, stirring and moistened mixture of raw materials, flux and calcium sulfate is subjected to briquetting or pelletizing. Agglomeration of the batch provides a reduction of mechanical entrainment of the charge and increases the content of germanium sublimates. In addition, during the removal of a mixture of gases and fumes, air is additionally introduced into the gas stream to oxidize germanium monosulfide vapors and gaseous impurities in order to irradiate the oxidized product.

The use of pyrometallurgical technology allowed to obtain through extraction of germanium from raw to concentrate at the level of 85–90 %, which is higher than the world level, without the formation of harmful effluents. In particular, chemical methods that create environmental problems are used abroad to extract germanium from coal combustion products. The final stage of the technology is the production of germanium concentrate. The quality of the latter is regulated by the technical conditions [2]. Concentrates are divided into two types: poor (BCG grades 1–3) with a germanium content of 0.3 to 5 % and ordinary (CG grades 1–5) with a germanium content of more than 5.0 %. The main requirements for BCG are: moisture content of not more than 4 %, and grain size-not more than 0.2 mm. for concentrates CG (grade 5) is limited to sulfide sulfur content – 0.2 %, and grade 4 and less – 0.1 %. In addition, in grades below CG grade 5 limited arsenic content – no more than 4.5 %, and the grain size should not exceed 0.5 mm. An important feature of the requirements for concentrates is the method for determining the germanium content: measurement of opening in hydrochloric acid. Undisguised germanium is not paid by the consumer and is considered a loss to the manufacturer.

Processing of germanium concentrates in Russia is focused on two enterprises: Germanium and Applications Ltd (production in Novomoskovsk, Tula region) and Germanium OJSC (Krasnoyarsk).

Germanium concentrate is obtained from primary raw materials, were subjected to hydrochloric acid decomposition in the presence of sulfuric acid and chlorine at 110–125

°C with stripping $GeCl_4$ in the gas phase, condensation and purification of the resulting liquid germanium tetrachloride [2, 3]. At the end of the distillation cycle, the solution in the reactor is neutralized by adding lime. Eventually gypsum and chloride cake is the waste process and stored in the dump.

One of the conditions for obtaining high-quality germaniun products from at the lasting stages of production is the purity of the intermediate product. Technical tetrachloride is passed for cleaning, which includes stages: distillation of sulfuric acid, purifying the tetrachloride from impurities of organic nature and mechanical inclusions; solvent extraction as a preliminary stage of purification from impurity elements, mainly by arsenic; rectification – deep cleaning of the tetrachloride from arsenic and other impurities. The rectificate is transferred to hydrolysis for the production of germanium dioxide and germanium metal, or to additional stages of thermochemical purification and distillation in order to obtain high purity germanium tetrachloride for optical fiber [4].

At the end of the process the hydrochloric acid decomposition of the concentrate part of germanium (from 1 to 10 %) remains in gypsum and chloride cake in the form of insoluble and sorbing compounds, which reduces the recovery from the supplier of concentrate, but may be considered as a reserve for additional extraction of germanium at the consumer concentrate. With a full cycle of processing of primary raw materials (as in the technological scheme of Germanium and Applications Ltd additional extraction of germanium from the cake will increase through extraction. In both cases, it seems appropriate to develop a technology for processing cake with the extraction of germanium.

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2. Experimental Part and Discussion of Results

To solve this problem, it is necessary to study the physical and chemical properties of gypsum and chloride cake. For this purpose, using modern techniques and equipment [5–9], including the use of equipment of the Central Committee "Ural-M", experimentally studied the physical and chemical properties of waste. To determine the chemical structure of IP-used the x-ray fluorescent spectrometer "S4 Explorer", the phase composition x – ray diffraction-Tomer "XRD 7000C", granulometric composition of the laser device "ANALYSETTE 22 NanoTec", specific surface area – gas absorption analyzer "TriStar 3020". The derivatogramma was shot on the Q-1500 device in a ceramic crucible in the air atmosphere.

For comparison in Table 1 shows the composition of the materials obtained during the processing of germanium concentrates from Sakhalin coal in Germanium OJSC (Krasnoyarsk) and Pavlovsk lignit in Germanium and Applications Ltd.

Phase chemical analysis found that all sulfur in both samples is a part of the sulfate ion. The main component of the sludge is the hemihydrate of calcium sulfate $CaSO_4.0.5H_2O$, which is confirmed by x-ray diffraction (Figure 1), and calcium hypochlorite. The latter is a corrosive and corrosive substance with a strong oxidizing effect. It belongs to the 2nd hazard class (highly hazardous substances) [10].

On derivatogram (Figure 2) shows that heating previously dried sample of the filter cake 1 is accompanied by two endothermic effects corresponding to the two in consecutive stages of dehydration: 110 °C – remove free moisture, when 145–168 °C –

Table 1: Elemental composition (%) samples cakes Germanium OJSC (cake 1) and Germanium and Applications Ltd (cake 2).

Element	Cake 1	Cake 2	Element	Cake 1	Cake 2
Ge	0.257	0.200	Pb	0.540	0.200
As	0.870	0.014	Ca	18.930	12.350
Fe	3.900	0.150	Mg	1.910	0.350
Cu	0.250	0.025	Mn	1.150	0.100
Ni	0.070	0.001	S	9.100	7.600
Co	0.050	0.001	Cl	1.380	6.450
Zn	4.160	0.050	SO_4^{2-}	27.290	22.800

removal of 0.5 molecules of water – hemihydrate sulfate of calcium and hypochlorite, with corresponding loss of mass of 13.1 and 12.9 % [11].

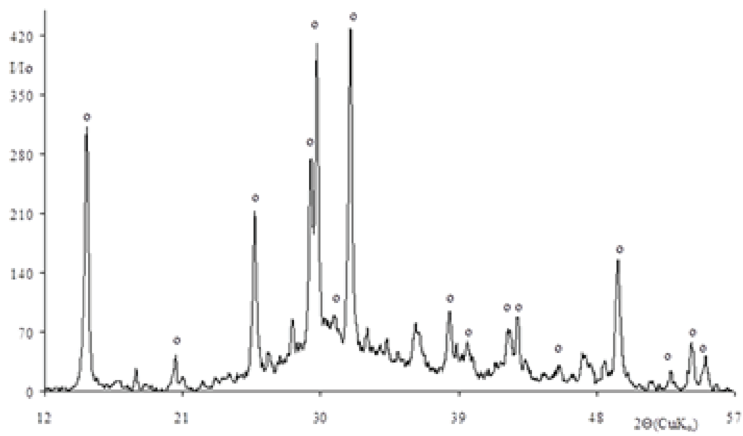

Figure 1: The diffraction pattern of the cake 2. Marked with the phrase: o – $CaSO_4 \cdot 0.5H_2O$, unmarked – $Ca(OCl)_2$.

The same applies to the presence of other impurities (table 1), then of these arsenic, zinc and lead in cake 1, and chlorine in both samples present significant challenges for the development of germanium recovery technology. Assuming, as in the monograph [4], that the undiscovered part of germanium in the concentrate is compounds or solid solutions with silicon dioxide, an effective technology should include their reagent high-temperature treatment [1]. Referring to the high sulfur content are the most suitable processes by sublimation of monosulfide, the oxidation of monosulfide in the gas phase to germanium dioxide and the capture of enriched product in the standard dust removal apparatus. It is obvious that to separate germanium from the other components and reduce pilipinos, technology should enable the operation of sintering. The necessary parameters can be selected taking into account the granulometric composition of the material (Figure 3).

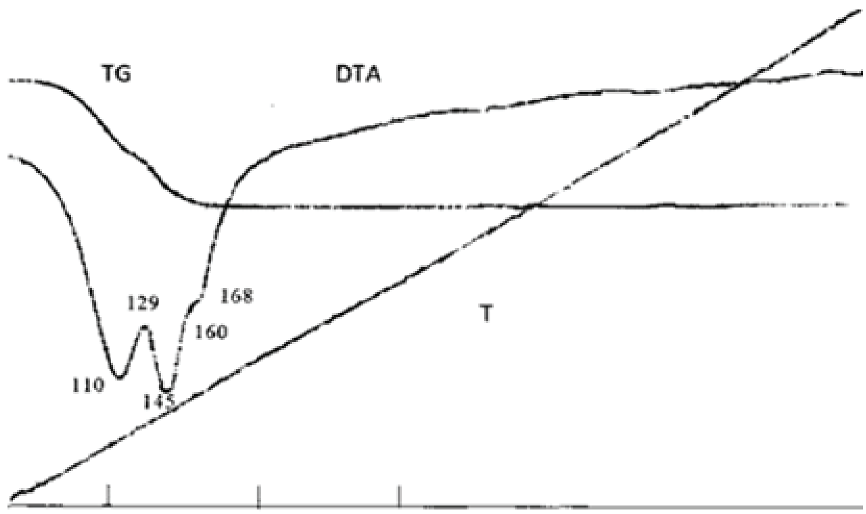

Figure 2: Derivatogram of the sample cake 1.

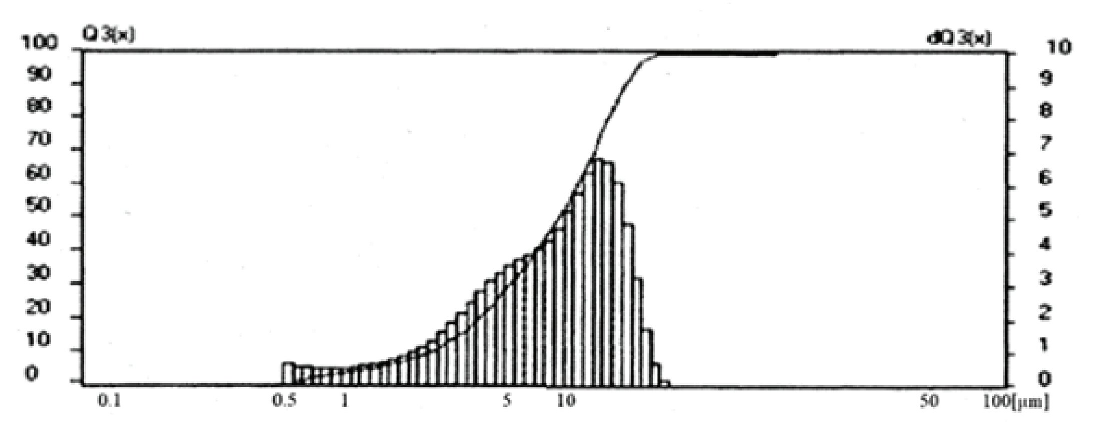

Figure 3: Particle size distribution in the cake 2.

Granulometric composition of cake 2 (Figure 3) characterized by high dispersion. With an average diameter of 12 μm, all particle sizes are in the region of 0.5–15 μm. The distribution of particle sizes is shifted in область10–15 μm, and the area of the particles less than 3 μm is not more than 10 %. The high dispersion of cake 2 is reflected in the specific surface area, which is 23.7 m^2/g.

As a result of researches it is established that wastes of chemical processing of germanium concentrates are environmentally dangerous products and have to be disposed preferably with germanium recovery.

Research results indicate possible ways of waste disposal. The presence of sulfate hemihydrate with high dispersibility can be considered as sulfidization component and a binder to produce agglomerates of the material after pre-reducing the moisture level to 20–25 %. In addition, recycling should be combined with the processing of silicate waste produced by germanium compounds, for example, with slag of layer combustion or electric smelting [1].

The performed research can serve as a basis for further development of perspective utilization of wastes of chemical processing of germanium concentrates in order to increase through extraction of germanium and environmental safety.

3. Summary

1. Given the conditions of the waste chemical processing of the germanium concentration (gypsum and chloride cakes) on two Russian companies.

2. With the use of modern methods of the elemental, phase and granulometric compositions of the two samples gypsum and chloride cakes of Germanium OJSC and Germanium and Applications Ltd, processing of germanium concentrates of various domestic and foreign enterprises.

3. It was found that the composition of the cakes of Germanium OJSC, except for germanium, significantly differ from the cakes of Germanium and Applications Ltd by the presence of noticeable amounts of impurities. At the same time, the main phase components in both cases are calcium sulfate semihydrate and calcium hypochloride.

4. The granulometric composition of cakes is characterized by high dispersion. With an average diameter of 12 μm, all particle sizes are in the region of 0.5–15 μm. The distribution of particle sizes is shifted in область10–15 μm, and the area of the particles less than 3 μm takes no more than 10 %. The high dispersion of cake 2 is reflected in the specific surface area, which is 23.7 m^2/g.

5. Derivatografic study found that heat treatment of the cake of custom is given by two endothermic effects corresponding to two consecutive stages of dehydration at 110°C (removal of free moisture), 145–168 °C (removal of 0.5 molecules of water) of the hemihydrate of calcium sulfate and the dissociation of hypochlorite with corresponding loss of mass of 13.1 and 12.9 %.

6. The identified areas of research to develop technologies for efficient recycling of the chemical processing of germanium concentrates.

Gratitude

The work was performed according to the state task of IMET UrO RAS.

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