CENTRAL RED PHOSPHORITES ENRICHMENT METHODS. REVIEW.
Kholiyorova O.J., Diyarov Kh.D.

[1,2]Department of Chemical Technology, Termez Institute of Engineering and Technology. Termez 100190, Uzbekistan

Abtract.

This analytical article provides detailed information about the methods of beneficiation of Central Kyzylkum phosphorites and the effect of physico-chemical factors affecting its productivity. The properties of thermal beneficiation of phosphate ores and other beneficiation were studied. Also, some information about the advantages and disadvantages of this enrichment is given.

Keywords: Central Kyzylkum phosphorites, beneficiation methods, Phosphate ores, thermal beneficiation.

Introduction

The theoretical aspect of flotation beneficiation of phosphate ores is presented in [1]. The results of the analysis presented in [2] of various methods of flotation enrichment show that, theoretically, it is possible to obtain 33% R2O5 raw phosphate from pure phosphorus-bearing minerals in three different ways.

Flotation of carbonate ores with the help of fatty and silicic acid. In this method, silicon oxide is first separated and then carbonates are separated. Amorphous collectors are used for selective separation of carbonate and silica (sodium salts of normal-alkylaminopropionic acid).

The carbonates are flotation using the above reagents and then selective flocculation and flotation using excess fatty acid. Among these methods, the extraction rate of P2O5 is better using methods 2 and 3.

A flotation device was developed without adding additives to phosphate raw materials. [3] The first device works in a dry method. The main node of this device is a multi-level classifier. This ensures that the materials are clearly separated. Productivity of the device is from 5 to 50 tons/hour. This device has been tested in Tunisia, Morocco and other countries.

The second device works on the basis of water flow[4]. Phosphate raw materials are converted into pulp. The water flow is affected at a speed of 100 m/sec and a pressure of 56-175 atm.

The mixture of crushed phosphorite, soil and sand is separated using methods known to us.

Several studies have shown that the addition of sodium additives increases the efficiency of the flotation process. American researchers found that the flotation process of phosphorites is improved by adding liquid glass.[5] studied in the literature by adding liquid glass and soda.

A flotation scheme (21% P_2O_5 and 8% Fe_2O_3) has been developed in which the ore is extracted from the washed concentrate in laboratory conditions. As a result, a high-quality concentrate with a low content of iron oxide (28% P_2O_5 and 3% P_2O_5) was obtained, allowing to obtain superphosphate. When the ore flotation process was studied, the washed concentrate was obtained, which made it possible to separate iron and phosphates from the ore when a mixture of liquid glass and soda was added during the flotation process.

Similarly, a mixture of glass and alkali gave good results[6].

High silicic acid and natural phosphates containing Ca and Mg are subjected to anionic flotation in the 2nd stage. In the 1st stage, the main part of the silicic acid is separated during the flotation process.

As a reagent, carbonic acid is used together with sodium silicate and alkali at pH 3-10.5.

The enriched phosphate (pH 4.54-5.8) containing Ca and Mg carbonate is treated with a solution of phosphoric acid. The resulting concentrate undergoes secondary anionic flotation, where Ca and Mg carbonates are separated.

In contrast to previous studies, organic acids are added together with alkali and acids in the process of phosphorite flotation [7]. In the flotation of phosphorites[8], sodium sulfide is an effective precipitant. As a result, the time of the flotation process is significantly reduced.

[8] also studied the effect of alkali metal salts on the flotation process.

In [9], the process of flotation beneficiation of phosphorite ores from the Khazar mine of Pakistan is described. The flotation process includes the following stages. Grinding the ore in the mill and flotation to get rid of the siliceous part to

obtain enriched calcined phosphorite. Various anionic collectors are used in the flotation process.

The main indicators of the process have been established. Optimal conditions for pH and liquid-solid phase ratio are established. (26% P_2O_5, 27.8% SiO_2) (33% P_2O_5, 19% SiO_2) concentrate was obtained. The output of P_2O_5 was 82%.

N.T. Sapkov and M.R. Oryol developed a technological scheme for the enrichment of raw materials with ore containing phosphorite 22%, calcium 27%, quartz 11% anhydride 10%, feldspar 7%, earthy minerals 4%, iron hydroxide 1% [11] . This technological scheme includes the following. Grinding of raw materials, followed by washing of soil sludge, flotation of calcium, additional flotation of phosphorite ore separated from sludge. Oil products are used as a collector in the flotation process. The amount of P_2O_5 in the obtained phosphorite concentrate is 21.8%.

The conducted studies developed a method of obtaining superphosphate from the concentrate obtained as a result of chemical flotation beneficiation of Kingisep phosphorite ore [12,13].

When the obtained concentrate is treated with a small amount of sulfuric acid at a pH of 2-4, phosphorite becomes active due to the fact that the boron part of phosphorus is transferred from tricalcium phosphate to dicalcium phosphate. During the activation process, the crystal-chemical and structural properties of the precipitate change. As a result, it is possible to completely separate the part obtained in the next flotation. The solution contains 33-36% P_2O_5, from which a 15% P_2O_5 concentrate is obtained. As a result of processing this concentrate with phosphoric acid, we will be able to obtain a mineral fertilizer containing 38-41% P_2O_5 and 19-21% aqueous P_2O_5.

The literature [14] provides information on magnetic processing in improving the flotation process of phosphorites. The literature analysis shows that enrichment of Central Kyzylkum phosphorites by flotation method is not effective.

For example: as a result of mechanical flotation beneficiation of Leroy ore, the yield of concentrate is 35.6%, the content of P_2O_5 is 22%, the yield of P_2O_5 extraction from the concentrate is 60.3% [15,16].

Phosphate ores can be divided into 4 directions depending on the method of thermal beneficiation and subsequent washing.

1. Without washing

2. Wash with water

3. Washing with salt solutions

4. Washing with acid solutions

Phosphorites, which mainly contain carbonates and organic additives, are thermally enriched. In order to reduce the ratio of CaO and P_2O_5, calcined phosphorite contains calcium and magnesium oxides.

A number of studies are devoted to the theoretical study of phosphorite ores [17,18]. In the literature, the rate of decomposition of only phosphorites in the temperature range of 600-1100C was studied. In this case, the heating rate is equal to 180 ºC.

The literature [19] shows the formation of OH-.. F bonds as a result of dehydration of phosphorite ores. It was found that as a result of incineration of phosphate ores, the processes of flotation, coagulation, filtration and improvement of product quality are intensified. As a result, it is possible to obtain water-soluble phosphorus mineral fertilizers from this ore [20.21]. They differ from each other in terms of ore content, burning conditions, phosphorite content.

In order to reduce the consumption of acid to obtain K3PO4 and mineral fertilizers from carbonate-bearing ores, ores are burned at 480-13700C, sieved, separated and other methods are used.

Several new methods of thermal enrichment have been developed [22.23].

[22] method is as follows. For beneficiation of phosphorite ores. The ore is crushed to a size of < 2 mm. After that, the phosphate and carbonate phases are separated from each other by the method of thermal enrichment. Depending on the type of mineral, the temperature is 350-750 oC for calcium ores and dolomite ores. 600-800 o C

The difference in the method is that the ores are crushed in ball mills, then separated into grades, and the part that does not pass through the sieve goes through re-stages. Thermal enrichment is carried out in rotary kilns. In this case, pulp and gas are supplied in a direct flow. After cooling, the phosphate is crushed in ball mills and then separated into grades, in which the particle size is <80-120 μm, and the phosphate part is completely separated during the crushing process. In this method, 90% phosphate concentrate is obtained.

In the [23] method, carbonate-retaining phosphates are burned. At the exit from the furnace, it is sharply cooled by air supply. Air carries away most of the mineral. Lime is extracted from it. The rest is crushed and returned to the oven.

Two-stage combustion has been developed by some researchers.

In order to remove organic impurities from phosphate ores and reduce the reactivity of sulfites present in it, it was recommended to oxidize the ore in 2 stages in ~10% oxygen atmosphere [24].

Two-stage oxidation of ore in 10% oxygen atmosphere was proposed to remove organic compounds from phosphate ores and reduce the reactive activity of sulphides present in it.

The first stage oxidizes 65% of organic matter at a temperature of 634-6670 °C, but sulphide rocks are almost unchanged at this temperature.

The 2nd stage is at a temperature of 656-740 0C, organic compounds are completely removed and the activity of sulphide minerals decreases on the surface of phosphorus ore.

In the first-stage incineration of phosphorous ores, in the state of balance of phosphorites (split time of phosphate ore in the incineration chamber <30 s), phosphate ore is stored for 5-10 minutes after incineration, then sent for cooling and separated by cooling.

Technologies have been developed based not only on ore beneficiation in hot-bed furnaces, but also on ore beneficiation in drum furnaces.

The technological parameters of the process of incineration of phosphate ores in hot-bed furnaces were studied [25]. At a temperature of 825 oC, the effect of the particle size in the range of -1 + 0.8-0.25 + 0.2 mm, the ratio of the layer height (L) to (D) at the bottom of the device (L: D = 2, 4, 6) organic compounds and the degree of mass enrichment of P_2O_5 in phosphorite ores, characterized by the quantitative ratio of carbonates, is determined by the velocity of solid particles UF (15; 22; 50 sec.-1).

It was found that the highest degree of enrichment was achieved when the particles were up to 50 mm (32.6%).

The variation of L:D values does not significantly affect the level of phosphorite enrichment.

The design of the incinerator has been slightly improved in comparison with hot-bed incineration and conventional incineration technology.

Phosphorite ores are kept at 900 ^{0}C during burning.

Air is supplied under the pressure of 2000 mm of water. After phosphorite enrichment, some phosphate species require the removal of calcium oxide to dilute the calcium modulus in the composition.

In [26.27] work, this is done by aqueous washing of various oxides.

The beneficiation of Indian ore containing 16.4% P_2O_5 was studied based on technological conditions.

Waste rocks are represented by dolomite and quartz. A multi-step enrichment process was proposed to produce concentrates containing up to 35.2% P_2O_5, 49.7% CaO, 0.4% Fe_2O_3, 0.5% Al_2O_3 and 3.3% F. Initially, the ore is crushed to a particle size of 4 mm and calcined at a temperature of 960 ± 100 ° C for 2 hours.

After the product is cooled to 4500, it is treated with water to quench the lime. To extract milk of lime, the pulp is passed through a 325 mm sieve. The concentrate is washed with water and dried. The yield of the concentrate is 74-78%. Enrichment of high-carbon phosphorites includes the processes of mechanical treatment of phosphorites, soil separation, calcination, washing and drying [27-30].

Washing is necessary to remove calcium and alkali metal hydroxides from the resulting product. The separation of CaO from calcination is based on the specific mass difference of CaO and fluorapatite. aqueous carbonation promotes the formation of $CaCO_3$ and facilitates the separation of CaO from fluorapatite. Unlike the above technologies, in this process, hot water is used for the enrichment of phosphorites[31]. Ore containing calcium carbonate is calcined, cooled and then fed to a "hot bed" reactor. Water or water vapor is sent to the reactor, which has a temperature of 482-871 0C at the entrance of the material. Calcium hydroxide formed during the quenching of calcium oxide is removed from the reactor together with exhaust gases. Enrichment is carried out at a temperature of 93-177 ^{0}C. For example. The particle size of heated ore (temperature 500-600) is 4 mm, the diameter is 3.05 mm, and the volume is 54.5 t/s. Other materials contain 10-15% CaO and 75.6-113.2 and 37.8-56.5 L/h of water are sprayed from the top and bottom of the material. The temperature in the reactor will be 167-170 ^{0}C[32]. As a result, ~ 50 tons/hour of enriched phosphate ore and 4.5 tons/hour of calcium hydroxide will be obtained, which contains materials with an average size of 65 mm particles. Calcium hydroxide is removed from the air leaving the apparatus. The rate of conversion of CaO to Ca (OH)$_2$ in the reactor reaches 85%, and 75% of Ca (OH)$_2$ is extracted

during the enrichment process. A slightly different technology is proposed in an English patent [33]. Phosphorite containing calcite (naturally or enriched) is calcined at a temperature of 850-9000 C, then the quenching of the formed CaO takes place at the expense of "moisture".

It is obtained only when the pH is kept constant until $Ca(OH)_2$ is completely converted to $CaCO_3$ when CO_2 gas is passed through the storage suspension. A study of washing heat-treated phosphorites with acid solutions was carried out.

In order to increase the amount of P_2O_5 and reduce the ratio of $CaO:P_2O_5$, natural phosphates containing carbonates (for example, the ratio of $CaO:P_2O_5 = 1.671$ with a ratio of H_3PO_4 of 100% phosphate, when taken in 3 kg of P_2O_5, 30.5% P_2O_5 and 51% CaO o containing phosphorite and calcined at a temperature of 9000C (the resulting material contains 36% P_2O_5 and 55.6% CaO with a ratio of $CaO:P_2O_5 = 1.541$) [34,35].

In addition, exposure to phosphorite with HCl (acid) allows leaching of alkaline-earth metal salts, and subsequent heating is effective.

Studies have been conducted on the removal of oxides of acid-forming gases. In a "hot bed" reactor, which moves phosphorous ores containing $_{H2S}$ against gaseous products, it is first heated to 40-950C, then heated to 650-100C and then cooled with air to 300-6500C. In other "hot bed" devices, ore is cooled in air and treated with H_3PO_4 solution (20-40% concentration, amount: 45.9 kg 0.9-9.0 kg, calcined ore 3 kg). The ratio CaO / P_2O_5 in the ore will be <1.5.

Enrichment of phosphate ore is carried out by calcining it with calcination, then dissolving calcium in NH4Cl solution and recovering calcium chloride waste; solution is carried out in the free oxides of Ca and Mg with NH_4Cl in excess of 3 times the stoichiometric ratio, pH 7.5 in the presence of a diluted solution of HCl, and oxidation of waste is carried out with an ammonium carbonate solution[36]..

Phosphorites of the Central Kyzylkum contain high carbonate minerals as well as organic compounds. The reason is that it depends on the layers of phosphorite and its depth. Therefore, thermal enrichment is widely used in the enrichment of phosphorites. Phosphorites, although not very high in organic matter, increase the stability of foams formed by acid decomposition, even relatively low levels of 4-6% CO_2 make it difficult to separate the insoluble residue. . According to the author [29], leaching of free CaO with water or saline solutions with thermo-chemical release of CO_2 can be an effective way to enrich these phosphorites.

Thermochemical treatment of phosphate ores improves the technological indicators of the process of converting phosphoconcentrates into mineral fertilizers with the participation of acid: reducing the consumption of acid when affecting raw materials, sharply reducing foaming, the way to reduce nitrate nitrogen in the production of nitrophosphates is not placed, the solubility of iron compounds changes and the quality improves.

The process of thermochemical enrichment of Kyzylkum phosphorites was studied by the researcher [37].

The main kinetic studies of beneficiation of high-carbonate phosphorites of Central Kyzylkum were carried out at (700-9000C) and the optimal conditions of beneficiation of raw materials were established: 800 0C, duration 45-90 minutes, degree of decarbonization - 98.5%. The RFA method showed a change in the chemical composition of the ore.

Samples of concentrates are obtained by washing heat-treated phosphorite samples with water and classifying them on sieves. The fractional composition of the phosphorite ore enriched by the thermochemical method of phosphorite is +5-7 mm, the composition of the obtained phosphoconcentrate sample contains 20-22% P_2O_5 (initial content 7.5%), 24-25.5 (13.6 %), 27-28.8% (20.5 %). The amount of P_2O_5 in the outgoing concentrate decreased from 79% to 93%. When the change of phase was studied using the X-ray method, it was concluded that ore enrichment was suitable for the production of complex fertilizer.

Taking into account the deep lowering of Kyzylkum ore in the process of splitting and beneficiation, with the attachment and aggregation of particles during processing, the development of incineration with pre-granulation of fine and medium-sized classes (class - 0.5 + 0 or -1 + 0 mm) came out [37].

In phosphorites, part of CO_2 is in the composition of endocalcite and phosphate mineral, in the form of fluorocarbonate apatite. during enrichment, CaO changes to the endocalcic state and is mixed with phosphorite grains. Carbonate fluoroapatite loses CO2 and changes to a phase close to that of fluoroapatite. It also forms CaO, which binds well with the phosphate mass.

Both forms of CaO are not lost by quenching and contact friction, resulting in a concentrate containing 12-14% CaO.

It was included in the combined technological scheme of enrichment of Kyzylkum phosphorites, 200 tons of concentrate was tested in semi-industrial

conditions and recommended for industrial sale. This scheme includes the processes of ore extraction, separation into components and subsequent incineration [32]. Later, calcium and waste rocks are removed from the production process by decomposition.

This process allows you to recover the main calcium content and a significant part of the fine quartz grains.

Part of the calcium contained in the phosphate grains remains in the concentrate. The product was produced at +40 (50) microns. A characteristic feature of this ore is that quenching and grinding methods are ineffective for separating the calcium oxide formed during calcination.

Since April 2001, a technological block for the production of thermally treated phosphoconcentrate has been put into operation in the city of Zarafshan, Navoi region.

After drying the richer part of Kyzylkum phosphorites (19.5-20% P_2O_5 and more) and the dry beneficiation method, the concentrate contains up to 23-24% P_2O_5 solution

Then the dried enriched concentrate is sent to the furnace brazing unit at a high temperature of 850-900 °C. Olmaliq OJSC Ammofos and calcified phosphate concentrate with 26-27% P_2O_5 content is sent to the Samarkand chemical plant for the production of Ammofos.

The thermochemical enrichment technology of Central Kyzylkum phosphorites in the city of Zarafshon has several serious disadvantages: the complexity of the technological scheme, high temperature and the use of a large amount of heat, which leads to an increase in the cost of the obtained concentrate. In addition, the percentage of chlorine in the composition of the incineration product is 0 It reaches 0.05-0.2%.

In the scientific literature, multi-stage chemical methods of enrichment of low-grade phosphorites are presented, of which the following classifications can be cited.

1. Various gases (oxides CO_2, SO_2, NO and NO_2)

2. Acids (HCl, H_2SO_4, H_3PO_4, HNO_3).

3. Different salt solutions

4. Organic compounds

Sulfur (IV) oxide is used in gas enrichment of low-grade phosphorites in many studies. For the first time, the possibility of using sulfur dioxide to enrich phosphorite. The phosphate part of the ore is practically unaffected. A number of works on enrichment of phosphorites with sulfur (IV) oxide were carried out by N. N. Treushenko, B. A. Koblev and others [37].

Conculision

The following disadvantages should be taken into account when using salts:

1. When ammonium salts are used at the boiling point of the solution, calcium and magnesium carbonates are completely converted to chlorides and sulfates within 6 hours, as a result, ammonia is released into the gas phase of carbon dioxide. These processes are hindered by high temperatures, long durations, and decomposition of ammonium salts and corrosion of equipment.

2. Poor filtration of the resulting pulps is a disadvantage of the magnesium phosphate and nitrate method.

3. In ammonium sulfate schemes, diluted solutions containing no more than 0.35% of $MgSO_4$ are obtained, which complicates their processing within 1-1.5 hours; a large loss of ammonia occurs in the first stage of the process.

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