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Regulation of the Structural and Chemical Properties of Minerals with the Help of Surface-Active Agents through Fine Grinding in Centrifugal Mills

T. S. YUSUPOV and E. A. KIRILLOVA

Institute of Geology and Mineralogy, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Koptyuga 3, Novosibirsk 630090 (Russia)

E-mail: yusupov@uiggm.nsc.ru

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Abstract

Structural and chemical changes in minerals during fine grinding are studied. It is established that mechanochemical treatment causes levelling of the surface properties and worsening of the separation of mineral substances by means of floatation. The problem was formulated to decrease defect formation and amorphization of structure during fine grinding. For tinstone and copper-nickel ores as examples, the effect of surface-active substances on the structural and chemical properties of minerals was studied; the possibility to slow down the generation of defects and decrease amorphization was demonstrated.

Key words: mechanical activation, surface-active substances, floatation, grinding, minerals, sulphides, tinstone

INTRODUCTION

Structural and chemical changes of the surface of minerals during activation grinding play an important part in the processes involved in the separation of mineral components and in ore dressing. They arise during grinding of fine mineral associations aimed at opening the polymineral aggregates and in the mills with elevated energy output – centrifugal, planetary, jet mills, and also in disintegrators *etc*. Along with opening of junctions, there is an increase in the number of broken and strained bonds, radicals, point defects, dislocations and other imperfections, which leads to an increase in hydration of minerals and decrease in their floatation ability. Due to mechanochemical processes, levelling of the sorption properties of minerals towards organic substances (floatation reagents) occurs, the gradient of separation characteristics decreases, and the selectivity of floatation (one of the main methods to separate fine mineral substances) worsens.

The goal of the present investigation was to develop grinding modes providing minimal structural-chemical changes along with a substantial increase in the efficiency of floatation separation.

There is an evident necessity to develop the methods that would cause a decrease in the formation of surface defects and amorphization degree during high-energy grinding of mineral raw material in the processes of ore dressing in the case when particle size is less than 40 mm. The formation of surface defects is hindered (inhibited) by adding surfactants (SAS) during centrifugal grinding. SAS are usually used as strength reducers and the agents to intensify dispersing, however, these properties of SAS do not manifest themselves during preliminary grinding of ores in ball mills [1, 2]. This is likely to be connected with relatively low mechanical action in ball gravitation mills, so that the migration of organic substances over the surface and into the depth of microcracks is insufficient. A crack shuts pressing out the SAS that had already been present along its boundaries. In high energy mills, in particular centrifugal mills, intensification of dispersing manifests itself in a more stable manner, because the cracks do not shut, and SAS penetrate to the mouth and deep into a crack.

The amount and dosage of SAS supplied at the stage of grinding are among the determinant factors of the dispersing process. The action of SAS as strength reducers and dispersing agents is exhibited with the small consumption of organic substances; an increase in the amount of SAS introduced for grinding causes the reverse effect: dispersing process slows down.

EXPERIMENTAL

Investigation of the effect of SAS was carried out for grinding tin dioxide (tinstone SnO_2) and iron sulphide (pyrrotine FeS_x) in the centrifugal planetary mill M-3. The reactivity of SnO_2 was determined on the basis of the degree of mineral dissolution in concentrated sulphuric acid. Surfactants were chosen on the basis of the principle of reagent selection developed for mineral floatation: oxyhydryl compounds were used for grinding oxides, while sulphohydryl compounds were used for grinding sulphides.

RESULTS AND DISCUSSION

The basis of slowing down the grinding process is the lubricating action of organic substances under mechanical action, especially friction. While a monolayer coating of the surface or even mosaic or island-like fixation are necessary for hydrophobization of minerals during floatation, substantially larger amount of organic substance is necessary to achieve multilayer coating of the surface in order to decrease deformation processes.

In the present work, we carried out mechanical activation of tinstone-containing sludge and established the braking effect, which was used to evaluate the possibility of hydrometallurgical recovery of tin. Mechanical activation is known to enhance the chemical activity of almost all the minerals, including non-yielding ones, so that they may become soluble in aggressive environment [4, 5]. In particular, acid-resisting tinstone after treatment in the centrifugal mill is almost completely soluble in hydrochloric acid due to a decrease in crystallite size and eth growth of microdistortions in the structure of the mineral (Fig. 1). On the basis of calorimetric measurements for mechanically activated tinstone, we also established the proportional dependence between the reactivity of the mineral and the heat of its dissolution in HCl. The data obtained for different samples substantially exceed (by 25–50 kJ/mol) the enthalpy of the reaction of dissolution for crystal SnO_2.

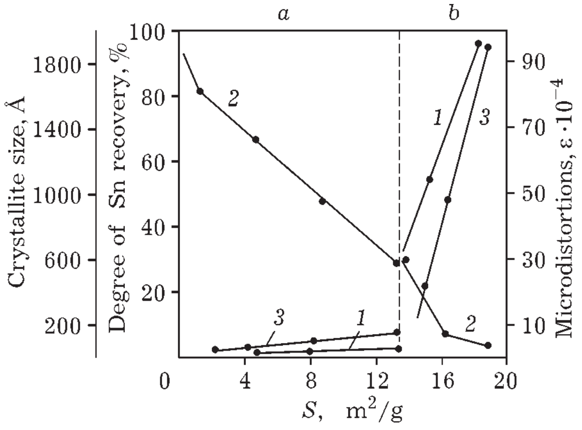

Fig. 1. Effect of the treatment of tinstone in SMB mortar (*a*) and in centrifugal mill M-3 (*b*) on the physicochemical characteristics of the treated material: *1* – degree of tin recovery into solution; *2* – crystallite size; *3* – value of microdistortions.

Along with this, mechanical activation of the indicated sludge product after floatation allowed us to transfer not more than 20 % of tin into the hydrochloric medium, which is connected with slowing down the amorphization of particles by residual coatings of floatation reagents, in particular sodium oleate. The removal of residual reagents by treating the sample with ethanol before mechanical activation allowed us to increase the degree of amorphization and hence the recovery of tin to 91 %, and the addition of the abrasive material (quartz) into the mixture for mechanical treatment allowed us to achieve the limiting value of SnO_2 solubility – 100 %. This fact was confirmed by the special addition of oleic acid into the mixture for mechanical activation. One can see in the data presented in Fig. 2 that the solubility of SnO_2 in HCl sharply decreases with the addition of the fatty acid reagent.

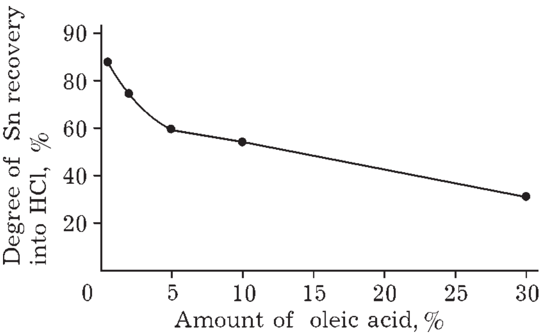

Fig. 2. Effect of the amount of oleic acid on the degree of tin recovery into HCl solution during mechanical activation. Activator mill M-3, treatment time 30 min, in the air.

An example of fine grinding with opening of the junctions before floatation concentrating can be tin-arsenic sludge from the Novosibirsk Tin Plant JSC (NTP). The sludge contains Sn 0.44 % and As 14.25 %. For the separation of tinstone-arsenopyrite association, sodium xanthate was chosen as the reagent instead of oleate. This is connected with the fact that the sludge contains larger amount of arsenopyrite than tinstone. In addition, for the efficient transformation of sulphide into the valuable product, it is reasonable to conserve its structure under depression of tinstone floatation. Tinstone floatation was not observed in this situation.

Centrifugal mill M-3 with metal balls 22 mm in diameter was used in experiments. The duration of treatment was 20–180 s. Treatment was carried out in aqueous medium (the ratio of solid to liquid to ball mass was 1 : 0.5 : 0.25).

TABLE 1

Granulometric composition of the sludge product from NTP before and after grinding in centrifugal mill M-3

Fraction size, mm	Yield of fractions, %		
	Initial sample	After treatment in M-3 for, s	
		20	90
+0.2	4.3	–	–
−0.2+0.1	27.0	4.8	0.5
−0.1+0.074	7.2	2.2	0.2
−0.074+0.04	17.5	11.2	8.2
−0.04+0.02	17.4	27.0	16.5
−0.02+0.01	16.0	37.5	51.4
−0.01+0.005	6.2	10.2	15.0
−0.005	4.4	7.1	8.2
Total	100.0	100.0	100.0

The weighed portion of material under treatment was 200 g. Floatation was carried out at pH 4.5, which was achieved by using H_2SO_4 and adding $CuSO_4$ (200 g/t) as the activator of sulphides, while the floatation reagent was butyl xanthate (100 g/t).

The results of granulometric analysis of the initial and ground products are presented in Table 1. One can see that after activation for only 20 s the particle size of the material almost completely corresponds to the floatation value (<0.074 mm), while after 90 s the major particle size is less than 0.04 mm.

The changes of Sn content of the chamber product depending on grinding time are shown in Fig. 3. One can see that with an increase in dispersing time the Sn content of the chamber product increased from 0.33 to 1.98 %. This is the evidence of a substantial increase in the opening of sulphide-tinstone junctions during fine grinding.

The concentrate with Sn content about 2 % may already be treated using the fuming process because the amount of As after floatation concentrating using fluorides and floatation gravitation decreased to 0.25 %. So, even these low-grade sludge can be used to recover the concentrate suitable for obtaining tin. This is also evidenced by the results of semi-industrial experiments at the developmental test plant of NTP.

Along with opening of junctions, the fine grinding of sludge involves removal of the technogenically modified surface layers of minerals, which results in the intensity of arsenopyrite reflections (Fig. 4). It is these factors that define the increased separability of minerals with the transformation of FeAsS into a valuable product. One can see in the data pre-

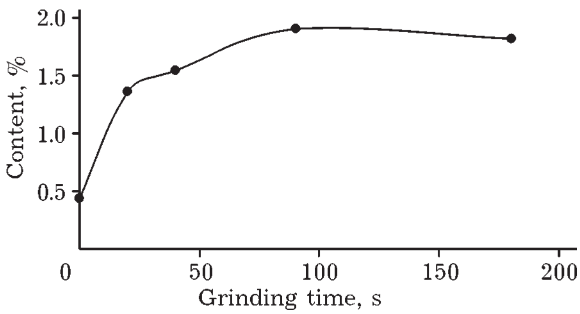

Fig. 3. Effect of fine grinding on tin content of the concentrate (chamber product of floatation).

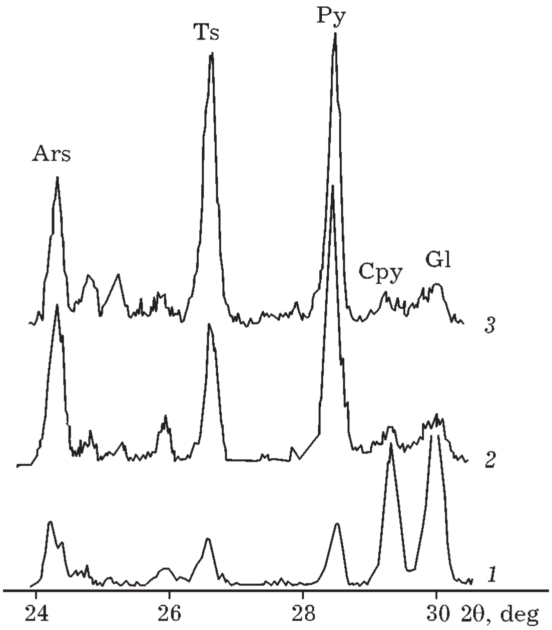

Fig. 4. Fragments of X-ray diffraction patterns of the chamber products of floatation of tinstone sludge: *1* – without grinding; *2*, *3* – after preliminary grinding for 20 (*2*) and 90 s (*3*). Ts – tinstone, Ars – arsenopyrite, Py – pyrite, CPy – chalcopyrite, Gl – galena.

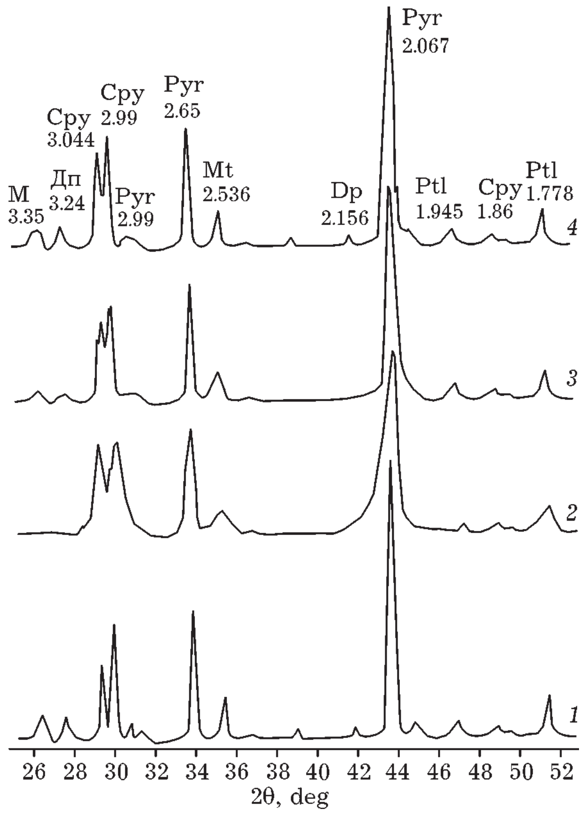

Fig. 5. X-ray diffraction patterns of pyrrotine concentrate: *1* – initial sample, *2–4* – after grinding for 5 min in aqueous medium in grinding activator (*2*), with the addition of butyl xanthate in the amount of 1500 (*3*) and 5000 g/t (*4*). Pyr – pyrrotine, Cpy – chalcopyrite, Ptl – pentlandite, Mt – magnetite, M – mica, Dp – diopside.

sented in Fig. 4 that the structure of SnO_2 becomes more perfect but the use of xanthate promotes activation of floatability, mainly for FeAsS.

The results of fine grinding of the sulphide ore from the Talnakh deposit also provide evidence of the possibility to decrease amorphization of the structure with the addition of floatation reagents into the mixture for dispersing. This effect is especially clearly exhibited with increased reagent consumption (Fig. 5). For example, the degree of pyrrotine amorphization is 28 % after grinding for 5 min in aqueous medium without adding a floatation reagent into the mill, while the addition of butyl xanthate in the amount of 1.5 kg/t causes a decrease to 19 %. With an increase in the reagent input to 5 kg/t the amorphized part of pyrrotine structure is only 9 %. With smaller reagent input corresponding to floatation, the change of the degree of amorphization does not exceed 1 %, but even this level of defect content has a strong effect on the floatation process. However, it is more informative to detect such small changes of structure by means of X-ray electron spectroscopy (XES) but not by means of X-ray phase analysis (XPA) [6].

The decrease of structure amorphization is exhibited to a higher extent in chemisorption of SAS in comparison with the physical form of interaction between the reagent and the mineral. In this aspect, it is interesting to study the processes of mineral amorphization during grinding extremely finely ingrained ore from the Talnakh deposit (Krasnoyarsk Territory); the procedure of their concentrating involves the supply of reagents into the mill. At the OJSC MMC Norilsk Nickel, the methods involving mechanical activation were included into processing for the purpose of increasing the extraction of valuable components from stale pyrrotine products.

The established decrease in amorphization in the presence of SAS with an increase in mineral separability, as the new section of the chemistry of surface-active substances, is at the start if its development. It is necessary to carry out thorough investigations of the efficiency of the use of special organic substances possessing lubricating action and selectively fixing at separate minerals, depending on the kinetic and mechanical factors under the action of high-energy treatment of substances in mills.

CONCLUSION

The effect of SAS on fine grinding of minerals in centrifugal mill was studied. It was established experimentally that the introduction of organic floatation reagents into the process promotes the change of the crystal structure of the mineral. For the minerals of tinstone and copper-nickel ores as examples, we demonstrate the routes to decrease defect formation under mechanical action for the purpose of increasing the selectivity of separation of mineral components.

The investigation performed by us broadens the notions of the action of organic substances for grinding of minerals, and opens the new possibilities for selective grinding with the conservation of surface structure as an important condition for increasing the efficiency of ore dressing.

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