EXPERIMENTAL STUDY OF IRIDIUM DISTRIBUTION IN HYDROTHERMAL SYNTHESIZED SULPHIDES FE, CU, ZN, PB WITH USING OF RADIOISOTOPE ^{192}Ir

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Experiments on hydrothermal synthesis of iridium containing sulphides of -Fe, -Cu, -Pb and -Zn with using of a radiotracers method [1] were made. The isotope ^{192}Ir was used as radioactive «label». Autoradiography was used as a method of registration of isotope ^{192}Ir in the synthesized minerals. The experiments were built in steel autoclaves with titanium bush V=55 см^3, at P = 500 bars, which was set on PTX diagram for aqueous solutions NH_4Cl. Temperature of a hydrothermal crystallization was set by VRT-3 with accuracy ±3°C and was equaled to 400 °C and 500 °C (two series of experiments). A gradient of temperature between the upper zone and lower was 14 °C. Time of experiments was from 100 till 1000 hours. Three experimental systems were generated with the purpose of synthesis of pairs of sulphides: Fe-Pb, Fe-Cu and Fe-Zn. The mixture was made from especially pure elements in stoichiometric proportions, typical for pyrite, galena, chalcopyrite and sphalerite. Solution of chloride of ammonium 2,06 M was as the working solution. Quantity of entered iridium varied from 11 ppm up to 74 ppm concerning an initial hinge of fitting of a blend (P=10 g) and was added in a blend as hydrochloride solution $Na_2{}^2[IrCl_6]^2$ c Ph=3,5. Water-soluble compound of iridium was received by a method of chlorination of metallic Ir, previously «marked» by a radionuclide ^{192}Ir on reaction $^{190}\text{Ir}\ (n, \gamma) \rightarrow {}^{192}\text{Ir}$. A plate of iridium was irradiated in a channel of a nuclear reactor with resonant neutrons. The radionuclide ^{192}Ir is also beta emitter with 74.4 days of half-life that has allowed to using a method of a beta-autoradiography for determination of a spatial distribution and forms of presence of iridium in the synthesized minerals. The registration of a beta-radiation was made with usage of an emulsion for nuclear researches such as MR and film for an autoradiography such as AF.

As a result of experiments the crystals and polycrystallic aggregates of pyrite, pyrrhotite and galena were obtained for Fe-Pb system; pyrite, chalcopyrite, bornite, chalcosine and pyrrhotite were obtained for Fe-Cu system; pyrite, pyrrhotite, ferriferous sphalerite and kleiophan were obtained for Fe-Zn system.

It was determined that all quantity of iridium, introduced in experimental systems, concentrates in the synthesized sulphides. The solutions and titanium bushes did not contain iridium. The enrichment by iridium of external surface of separate large crystals or polycrystallic aggregates is character of a spatial distribution of iridium in the synthesized sulphides. The internal parts of crystals and aggregates of sulphides did not contain iridium. And such type of distribution is marked as a matter of fact for all sulphide minerals: pyrite, chalcopyrite, bornite, pyrrhotite, galena, sphalerite. Own minerals of iridium in the synthesized sulphides are not detected, as by the data of an autoradiography (the points of maximum blackening on nuclear emulsions are missed), and as at analyzing on a scanning electron microscope. In infrequent cases the ultra dispersible inclusion - concentrators of iridium, which structure did not manage to be established, are marked.

As a result of the made experiments is established, that the iridium isn’t included in structure of any of the synthesized minerals, but it is concentrated on a surface of growing crystals and polycrystallic aggregates, that is on the crystal - solution boundary. The similar character of a spatial distribution of iridium between sulphides and solution corresponds to adsorption equilibrium. For the evidence of this supposition the type of iridium distribution in a layer on boundary sulphide-solution on the part of solution and on the part of a crystal was analyzed. It’s established, that the distribution curves of iridium on boundary sulphide - solution (site 1) have asymmetry: more flat gradual increase of iridium concentration from solution to a sulphide surface, in comparison with a surface of sulphide - near-surface part (site 2) of a crystal. Curves of concentration distribution of iridium on sites a surface of a crystal - solution and surface of a crystal - near-surface area of a crystal were built by the method of approximating. It’s established, that on a site 1 the changing of iridium concentration is described by an equation with squared cross correlation (R^2) 0.966: $y = y_0 + A_1 e^{-x/t_1} + A_2 e^{-x/t_2}$. According to the Hall theory [2-4], the effective value of a coefficient of distribution depends on growth rate and is described by expression, which characterizes distribution of an addition in a growing crystal in case of adsorption equation: $k_{eff} = k + (k_{ads} - k)e^{-\upsilon_{sl}/\upsilon}$, where are υ - growth rate, υ_{sl} - rate of transport of impurity atoms between a crystal and melt bordering to it; k_{ads} - coefficient of adsorption, k - coefficient of distribution (k_{eff}=k, when $\upsilon_{sl} > \upsilon$, and $k_{eff}=k_{ads}$, when $\upsilon > \upsilon_{sl}$). The dependence k_{eff} from growth rate is explained by formation of an adsorption layer on a boundary surface of phases. It is evidently, that the equations have the same exponential dependence. Then, according to the theory of the Hall [2-3], impurity atoms, in this case – of iridium, at first are adsorbed on interface and only then are entered into a lattice of a crystal. At low speeds of growth the adsorption layer goes before interface and is supported at the expense of a fast egress of a hard phase of atoms, which originally were adsorbed and are grasped by a growing crystal. It is confirmed by the analysis of a curve on a site 2 — a surface of a crystal - near-surface area of a crystal. Change of concentration of iridium here is described by a sigmoid curve that also corresponds to the theory of the Hall and distribution of concentration of an impurity in solid phase reactions [5].

As a result of the made experiments on hydrothermal synthesis of iridium containing of sulphides it is established, that the iridium is not included in structure of sulphides Fe, Cu, Pb, Zn. The distribution of iridium between solution and sulphide corresponds to adsorption equilibrium, instead of equilibrium between a volume of a crystal and a volume of solution. The growth rate of crystals was enough low – $3\ 10^{-6}$ - $3\ 10^{-9}$ cm/sec in our experiments. The concentration of iridium in sulphide minerals can be distributed enough uniformly in volume of minerals in the defects of crystal structure in the case of very high growth rate of crystals. It is occurred at the expense of fast overlap of an arising adsorption layer by mineral generating elements of a growing crystal. In case of a closed system it can be zoning forming. Evidently, that the coefficient of distribution (C_s/C_l) of iridium in an experimental system: sulphides Fe, Cu, Pb, Zn - hydrothermal solution is less than 1, but according to adsorption equilibrium in this case it is necessary to use not a coefficient of distribution, but effective coefficient of distribution dependent on coefficient of adsorption equilibrium [2-3].

The obtained data also indicate that the conclusions about the forms of presence and coefficients of iridium distribution obtained on the basis of total, instead of local analysis of coexisted phases, cannot correspond to actual values.

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