MODELLING OF INTERACTION THE DRAINAGE STREAM – THE CARBONATE BARRIER

Jurkevich N.V. (IGM SB RAS), **Lapitsky S.A., Alekhin Y.V., Frolikova M.A.** (Geol. Dep. MSU)
ovoin@mail.ru; Fax: (383) 333-27-92; Phone: (383) 330-95-36

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The waste products of mining industry containing high concentration of ore components as secondary well soluble minerals at interaction with seasonal waters become sources of acid drainage streams with the increased mineralization and extremely high concentration of toxic elements (Cu, Zn, Cd, Pb, As, Sb, etc.) [1]. Distribution of hyperacid streams with harmful chemical substances to an environment is prevented by the natural geochemical barriers located along the path of spreading of drainage [2 - 3]. Major of such barriers are bottom sediments of the rivers taking the drainage, soils in vicinities of tailing dump, clay and limestones in the accommodating rocks laying under the basis of dump [4]. The interaction of the ferriferous acid sulfate drainage stream following from under the tailing dump of waste products of Belovo zinc processing plant (BZP, Belovo, Kemerovo region) with natural limestone from a deposit of Novosibirsk region is simulated in this work.

The waste material is a clinker, which is a product of pyrometallurgical smelting of sphalerite concentrate of Salair lead-zinc plant (Kemerovo region). At present waste heaps contain over 600 thousand tons of clinkers of complex structure. The basis is provided with silicate glass, metals mainly contain as alloys, and there is a small amount of residual sulfides. The surface of heaps is covered by sulfate efflorescences containing Ca, Fe, Al, Mg with a touch of Zn, Cu, As. The drainage following from under the dump, is characterized by low values pH=3.4-3.6 and high Zn, Cu, Cd concentration in solution [5]. The purpose of work is an estimation of limestone neutralizing ability in relation to aggressive technogenic stream and capacity of a material to absorb Zn, Cu, Cd from a considered solution.

Process of a filtration of solutions is optimized with the help of Pekle similarity criterion to increase the efficiency of metals deposition on a carbonate geochemical barrier. Degrees of extraction of ore substance, accumulation on a carbonate barrier, dynamics of development of chromatographic fronts and capacity of absorption were estimated by the method of output concentration curves and the level-by-level analysis of matrix of columns. The number of experiments has been carried out on immobilization of metals from sulfate solutions on carbonate barrier to determine a limitative stage of migration. Three sulfate solutions filtered through 20 g of limestone fraction 0.1 - 0.25 mm in specially made glass columns. There were sulfate solutions (mg/l): Cu (5.4), Zn (4.5), Cd (1.6) in a column № 1; Cu (5.4), Zn (4.5), Cd (1.6), Fe (17 г/л) in a column № 2; solution leached from waste material of BZP (23 and 1 g/l Fe and Cu, 690 and 0.40 mg/l Zn and Cd) in a column № 3. The pH values were checked in filtrates within 34-76 days using potentiometry. The samples of filtrate were collected to measure the concentrations of Cu, Zn, Cd, Fe (AAS method). The reacted limestone divided into visually various layers and analyzed by XRF-SR method to detect metals concentration after carrying out of experiments. X-ray diffraction analysis was used to define mineral structure of samples.

Results. Column N 1

After initial neutralization of a solution and decreasing of metals concentrations on 2 orders low pH = 1.20 values and contents of elements at a level of initial is fixed in filtrate by the 44th day. Quick decrease of pH values is bound up with parietal filtration of an acid solution, its infiltration through the hollowed out channels and formation of gypsum $CaSO_4*2H_2O$ crust around the grains of a limestone. In all cases there is no effective interaction of a stream with carbonate material. The filtration coefficient (Kf) is equal 1 cm/day on the average. Capacities of absorption counting upon 1 g limestone amount (mg): 0.0049 Cu, 0.0037 Zn, and 0.0015 Cd. The basic part of metals passes in the lower front of a column and concentrates in a layer of limestone (g/t): 64 Zn, 40 Cd, and 43 Cu.

Column N 2

The ferriferous sulfate solution is filtered with Kf = 0.5 cm/day, neutralized only up to subacid value pH = 5.60, metals concentration decrease on 2 orders in comparison with initial maintenances. Low pH = 3.70, Zn and Fe concentrations at initial level, Cu and Cd contents below initial concentration on 1 order is fixed by the 11th day. The lowering of neutralizing and absorbing capacity of limestone is caused not only by formation of gypsum crust around of limestone grains, but also cementation of surface with iron (III) hydroxides. The sorption - sedimentation barrier concentrating metals due to sedimentation of insoluble carbonates and because of sorption of elements on compound of goethite FeOOH type is formed in the upper layer of a column. The concentration of Fe, Cu, Zn, Cd in this horizon are amount 6.5 %, 210, 73, 32 g/t accordingly. Absorption capacities of limestone are equal to (mg): 0.0059 Cu, 0.0040 Zn, 0.0017 Cd, 2.4 Fe counting on 1 g of limestone.

Column N 3

The solution leached from substance waste material is filtered through limestone with Kf = 0.2 cm/day, neutralized up to values pH = 7.50 - 8.10, concentration of metals in the beginning of experiment are reduced on 1-6 orders in comparison with an initial level. As well as in the previous case, sorption - sedimentation barrier concentrating the bulk of metals (g/t): Cu (4700), Zn (1700), Cd (6.2) and Fe (11 %) is formed on a surface of limestone due to sedimentation of Fe (III) hydroxides. The gypsum and secondary Fe sulfates such as jarosite $NaFe_3(SO_4)_2(OH)_6$ are formed in this horizon. The absorption capacities of limestone relatively to metals are equal to (mg): 9.3 Fe, 0.41 Cu, 0.27 Zn, 0.16 mkg Cd counting upon 1 g limestone.

Conclusion

The interaction of sulfate solution containing Cu, Zn, Cd, with limestone results in initial neutralization and decreasing of metals concentrations to the moment, when a ratio solution / limestone = 13/1. Then the surface of limestone becomes covered by gypsum and iron (III) hydroxide, the material loses efficiency, and the acid solution with initial concentration of metals is registered. The degree of neutralization proceeding does not reach also the first percent by calculations on a lump of limestone. The presence of a significant amount of iron in solution results in sedimentation of iron (III) hydroxides sorbing metals effectively on a limestone surface. The effective neutralization of a solution and decrease in concentration of metals on 1-6 orders is reached in comparison with initial contents only at enough low factors of a filtration (0.2 cm/day). The hydrolytic sedimentation of Fe (III) hydroxides on limestone causes formation of sorption - sedimentation barrier concentrating (g/t): 4700 Cu, 1700 Zn, 6.2 Cd 11 % Fe. The full chemical rebalancing of phases is not fixed even at small speeds of a filtration. That is absorption of metals occurs as chromatographic process without limiting sorption saturation and full proceeding of interaction of sulfate solutions with limestone. The main features of the mechanism of deposition of ore components are similar to processes of secondary accumulation in zones of oxidation and cementation of «iron hats» in sulfide deposits.

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