

**SULPHIDIZATION OF VALLERIITE  $x(\text{Fe,Cu,Ni})\text{S}\cdot y\text{Mg}(\text{OH})_2\cdot z\text{Al}(\text{OH})_3$   
IN  $\text{SO}_2$  WATER SOLUTIONS**

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Valleriite is a sulphide-hydroxide mineral with a mixed-layered structure. It has been found to be widely spread at the largest deposits of the Norilsk ore zone (Russia) as a product of the zonal hydrothermal metasomatic substitution of continuous sulphide ores (pyrrhotite, chalcopyrite, pentlandite) in gabbro-dolerite enclosing rocks [1, 2]. This type of valleriite-containing cupriferous ores is of industrial significance due to copper and nickel resources, moreover, it is essentially enriched in metals of the platinum group [3]. Direct flotation enrichment of these kinds of ores is characterized by low indications for extraction into a sulfide concentrate of copper and nickel (on the level of 40 – 60%) because of specific surface properties of valleriite and its close intergrowths with serpentine.

Chemical and mineralogical composition of the analyzed sample from the valleriite-containing ore taken at the Talnakh is shown in tables 1 and 2. According to the micro-X-ray-spectral analysis (device JEOL Flex Seam T566) the valleriite composition corresponds to formula  $[2.0(\text{Fe}_{0.57}\text{Cu}_{0.38}\text{Ni}_{0.025})\text{S}\cdot 1.31\text{Mg}(\text{OH})_2\cdot 0.37\text{Al}(\text{OH})_3]$ . With valleriite concentration in this type of ores on a level of 14% the share of “valleriite” copper reaches 55-60% from its total content. Platinum and palladium are present in the amount of 2.3 and 9.4 g/t ore, respectively.

**Table 1**

Contents of basic components of valleriite-containing ore (mass %)

Fe	Cu	Ni	Co	S(total)	CaO	MgO	MnO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Σ
19.0	4.1	1.35	0.027	12.9	6.18	17.7	0.065	16.7	4.78	82.80

**Table 2**

Contents of minerals according to mineralogical data (mass %)\*

Val	Py	Cp	Mag	Po	Pn	Serp	Pg	Ca	X	Σ
14.0	8.1	6.1	5.9	3.8	0.6	43.7	7.6	7.6	2.6	100

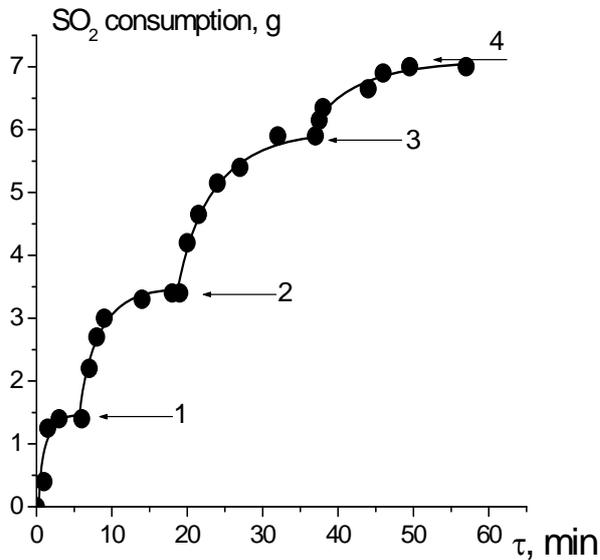
\* Val - valleriite, Py - pyrite, Cp - chalcopyrite, Mag - magnetite, Po - pyrrhotite, Pn - pentlandite, Serp - serpentine, Pg - plagioclase, Ca - carbonate, X - other ore minerals

The aim of the present investigation is to elaborate a method of directed valleriite sulphidization in hydrothermal conditions for producing new formed sulfides of copper and nickel with a high flotation capability. We are the first to discover that an intensive transformation of valleriite followed by a recovery of nonferrous metal sulfides and dissolution of Mg and Al hydro-oxides takes place in water solutions of sulphurous anhydride  $\text{SO}_2$  already at temperature 95°C and partial pressure  $P_{\text{SO}_2} = 0.1$  MPa. Sulphurous anhydride occurs as a residual and excessive component in the actual “Norilsk Nickel” Company (Russia) as a result of oxidizing roasting of nonferrous metal sulfide ores, which makes its usage quite accessible as a reagent in the offered hydrometallurgical technology.

The kinetics of valleriite ore interaction with  $\text{SO}_2$  dissolved in water was investigated at  $t = 90 - 95^\circ\text{C}$  using an apparatus for hydrothermal investigations, developed and created at the Institute of Geology and Mineralogy SB RAS with the reactor volume of 110 cm<sup>3</sup>. Ore lading consisted of 10 g with sample grinding in a laboratory disintegrator 150 A with 5 row finger-like rotors made of the W-Co alloy up to particle sizes less than 45 μm. The water-solid ratio was equal to 8. The stirring rate of the pulp in reactor was 2000 r/min in an electromagnetic turbine stirrer. Sulphurous gas was directed to reactor from the micro vessel where it existed as liquefied state ( $P_{\text{SO}_2} = 0.22$  MPa at 20°C) through a teflon pipe. This fact permitted to have the current consumption of sulphurous anhydride (about 7 g per test) recorded as to a micro vessel weight loss by an electron balance as exact as ±0.02 g. The consumption rate of  $\text{SO}_2$  was determined by its specified partial pressure  $P_{\text{SO}_2} = 0.1$  MPa which constant value was maintained by hand regulating the inlet valve on reactor based on the readings of the total pressure on manometer ( $P_{\text{total}} = P_{\text{H}_2\text{O}} + P_{\text{SO}_2} = 0.18$  MPa).

The consumption of  $\text{SO}_2$  when interacting with ore sample satisfies demands of the complex kinetic dependence with successive halts of the process at stages 1 – 4 (fig. 1). It is caused by a fast exchange interaction of sulphurous anhydride and calcite in the ore composition (7.8 % mass  $\text{CaCO}_3$  – tab. 2), which gives rise to an accumulation of carbon dioxide  $\text{CO}_2$  in the gas phase at its fixed total pressure.

To renew the basic sulphidization process of valleriite a leakage of the gas phase was carried out at the end of each stage up to atmospheric pressure. With the overall  $\text{SO}_2$  consumption equal to 7.1 g its losses during leakage don't exceed 0.9 g, if occurs mostly at the final stages 3 and 4 actually under a complete disappearance of carbonates.



**Fig.1.** Kinetics of  $\text{SO}_2$  consumption at its interaction with valleriite ore in water pulp. Experimental conditions:  $t = 95^\circ\text{C}$ ,  $P_{\text{total}} = 0.18 \text{ MPa}$  ( $P_{\text{SO}_2} = 0.1 \text{ MPa}$ ), liquid/solid ratio equal to 8; grain size  $< 45 \mu\text{m}$ . Arrows 1 – 4 correspond to the maximum level of total  $\text{SO}_2$  consumption at the end of each kinetic stage

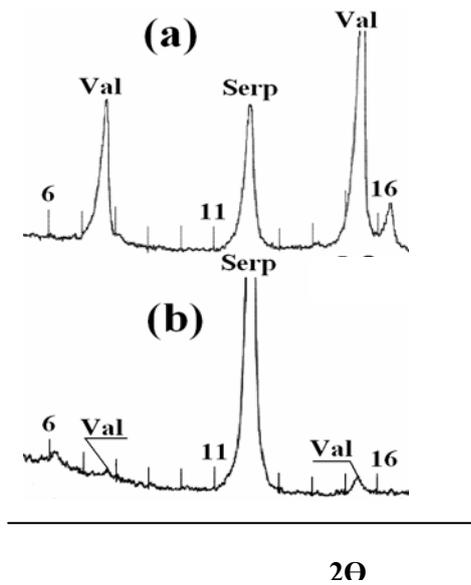
Contents of the main chemical ore elements in the solid phase and solution after experiment at a balance  $\text{SO}_2$  consumption - 6.2 g presented in table 3. Concentrations of dissolved Cu and Ni don't exceed 0.001-0.01 g/l in the process of creating an increased acidity of solutions ( $\text{pH} = 0.8-1.2$ ). It determines their practically complete recovery into a solid phase ( $\epsilon_{\text{solid}} \sim 100\%$ ). Cobalt in part enriches the solution ( $c = 0.004 \text{ g/l}$ ;  $\epsilon_{\text{solution}} = 12\%$ ). The total content of the nonferrous metals in a residual solid phase due to an intensive leaching of Fe, MgO and  $\text{Al}_2\text{O}_3$  (13.04, 7.95 and 1.52 g/l, respectively) rises from 5.48 up to 9.68%.  $\text{SiO}_2$  contents in the solid phase increase from 16.7 to 20.89% at its minimal transfer into solution (0.01 g/l). Sulphur content in residual solid phase increases from 12.9 to 34.1% at its concentration in solution 24.22 g/l (tab. 3). A distribution of various forms of sulfur into experimental products with its total quantity 4.34 g (initial and consumed) is the following: solid phase, S (sulphide) – 17.5%, S(el) – 25.0%; solution, S(polythionate) – 44.3%, S(sulphate) – 7.8%, S(sulphite) – 5.4%.

**Table 3**

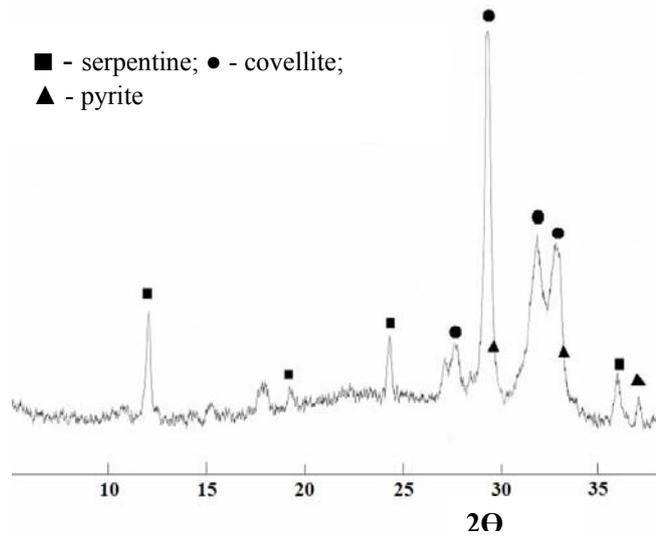
The content of chemical elements in the solid before and after the experiment (% mass, lines 1 and 2, correspondently) and their concentration in solution after the leaching process (g/l, line 3).

Line No.	Cu	Ni	Co	Fe	S	MgO	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$
1	4.10	1.35	0.027	19.00	12.90	17.70	16.70	4.78
2	7.24	2.40	0.039	11.16	34.10	15.30	20.89	4.36
3	0.001	0.01	0.004	13.04	24.22	7.95	0.01	1.52

The X-ray method established a presence of serpentine, elementary sulphur S (el) and gypsum  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  as dominating phases in the cake composition after ore leaching. Valleriite lines practically were not recorded (fig. 2). Lines of new formed of Cu and Ni sulfides as suggested products of valleriite conversion were absent within the limits of the method sensibility. They were detected only in a sulfide concentrate as the final product of cake separation using a sulfide flotation and extraction of elementary sulfur (fig. 3). Intensive lines corresponding to covellite  $\text{CuS}$  [JCPDS data cards PDF 76-1725] and pyrite  $\text{FeS}_2$  [PDF 71-2219] well reveal themselves in the absence of principal valleriite lines ( $2\theta = 7.8^\circ$  и  $15.5^\circ$ ) in the diffractogram of this product. In the case of absence of a nickel containing phase we suggest a nickel concentrating either in a mixed Cu-Ni sulfide  $(\text{Cu,Ni})\text{S}$  or in a new formed nickel containing pyrite  $(\text{Fe,Ni})\text{S}_2$  according to the mechanism of isomorphic mixing.



**Fig.2.** Fragment of XRD of valleriite ore in the initial state (a) and after its leaching (b). DRON-3 device, Cu K $\alpha$  radiation, Fe-filter



**Fig.3.** XRD for obtained sulphide concentrate, DRON-3 device, Cu K $\alpha$  radiation, Fe-filter

The transfer of copper and nickel into well floated forms results in an achievement of required technological indicators for extraction of nonferrous metals from valleriite-containing ore into sulfide concentrate according to the combined scheme of its treatment with a preliminary stage of valleriite sulphidization (tab. 4).

**Table 4**

Comparative indicators for contents and extraction of Cu, Ni, Pt, Pd out of valleriite-containing cupreous ore into sulfide concentrate according to common and combined scheme

Variant of valleriite ore enrichment	Contents				Extraction, %			
	% mass		g/t		Cu	Ni	Pt	Pd
	Cu	Ni	Pt	Pd				
Initial ore	4.0	1.3	2.3	9.4	100	100	100	100
Direct sulfide flotation	5.1	1.7	4.4	19.8	40.8	42.5	61.0	67.3
Combined variant	14.4	5.2	9.3	36.3	92.9	97.6	96.5	92.6
Technological effect of combined variant, %	+9.3	+3.5	+4.9	+16.5	+52.1	+55.1	+35.5	+25.3

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