



# Ultrafine particles in ground sulfide ores: A comparison of four Cu-Ni ores from Siberia, Russia



Yuri Mikhlin<sup>a,\*</sup>, Alexander Romanchenko<sup>a</sup>, Sergey Vorobyev<sup>a</sup>, Sergey Karasev<sup>a</sup>, Mikhail Volochaev<sup>c</sup>, Evgeny Kamenskiy<sup>a</sup>, Ekaterina Burdakova<sup>b</sup>

<sup>a</sup> Institute of Chemistry and Chemical Technology of the Siberian Branch of the Russian Academy of Sciences, Akademgorodok, 50/24, Krasnoyarsk 660036, Russia

<sup>b</sup> Siberian Federal University, Svobodny pr. 79, Krasnoyarsk 660041, Russia

<sup>c</sup> Kirensky Institute of Physics of the Siberian Branch of the Russian Academy of Sciences, Akademgorodok 50/38, Krasnoyarsk 660036, Russia

## ARTICLE INFO

### Article history:

Received 7 August 2016

Received in revised form 12 October 2016

Accepted 21 October 2016

Available online 24 October 2016

### Keywords:

Cu-Ni sulfide ores

Ultrafine particles

Mineral surfaces

Colloids

Beneficiation

Environment

## ABSTRACT

Nano-, submicro- and micrometer mineral particles may have an important role in beneficiation of metal ores and environmental impact, but their origin and characteristics are poorly understood. Here, we report data for the yield and the composition of fine fractions, and surfaces of several ground Cu-Ni sulfide ores studied using laser diffraction, scanning electron microscopy and energy dispersive X-ray analysis, X-ray photoelectron spectroscopy. Colloidal particles were characterized using dynamic light scattering, zeta-potential measurement, transmission electron microscopy and electron diffraction. The production of fines by dry milling was found to increase from about 0.01 vol.% to 0.2 vol.% for submicrometer particles and from ~0.5 vol.% to about 1.5 vol.% for particulate material less than 5 μm in the following order: Noril'sk disseminated low sulfide ore ≤ Noril'sk Cu-rich sulfide ore < Noril'sk valleriite ore < Kingash ore. For wet milling, the yield may be several times higher. Both surfaces of the milled ores and colloids were enriched in O, Mg, Si (largely as serpentine slimes) and depleted in sulfur, basic metals and iron, but colloidal valleriite, chalcocopyrite, and oxidized pyrrhotite were found in the respective supernatants too. Typically, the colloidal particles form aggregates with an average hydrodynamic diameter of about 1 μm and a smaller number of ~5 μm species, except for valleriite ore, which exhibits a single size distribution peak at 2.7 μm. Zeta-potential, which characterizes the electric charge of the particles and dispersion stability of colloids, changed from –25 mV for the low sulfide ore to about 0 mV for valleriite ore, and to +15 mV for Kingash ore. Poor flotation recovery of metal from Kingash ore and Noril'sk valleriite ore is suggested to be due to both the large quantities and positive charge of hydrophilic ultrafine serpentine and/or magnesium hydroxide minerals. Resistance to oxidation and hence stability against aggregation of copper-bearing sulfide colloids in waste waters is expected to result in a negative impact on the environment.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

The efficiency of processing of sulfide ores of base and precious metals depends not only on grade, chemical and mineralogical composition but also on the texture of the ore, including grain size, hardness, and intergrowth of sulfide and gangue minerals. It is also necessary to take into consideration particle size distributions of ground ores, which is difficult to predict from geological analysis and mineralogical characterization. Recovery of metal from sulfide ores commonly involves crushing and grinding the ore to the particle size ranging from 20 μm to 100 μm in order to liberate minerals before the separation. Flotation recovery of smaller sulfide particles usually decreases, mainly due to a slow bubble-particle attachment, and notable quantities of metals can be lost to the tailings (Albjanic et al., 2010; Feng and Aldrich,

1999; Johnson, 2006; Miettinen et al., 2010; Sivamohan, 1990; Subrahmanyam and Forssberg, 1990; Trahar, 1981). In practice, particle size distributions of milled ores are quite wide, comprising particles of both metal sulfide and gangue minerals ranging in size from micrometer through submicrometer to nanometer scale. These ultrafine particles can accumulate in water produced from the mill, increasing viscosity of slurries, being entrained into flotation froth, etc., or can deposit on mineral surfaces affecting their characteristics. Generally, these phenomena are weakly controllable and have a detrimental effect on the flotation performance (Bremmell et al., 2005; Edwards et al., 1980; George et al., 2004; Grano, 2009; Feng et al., 2012, 2016; Kirjavainen and Heiskanen, 2007; Miettinen et al., 2010; Peng and Grano, 2010; Pietrobon et al., 1997; Senior and Thomas, 2005). The ultrafine particles then go into metal concentrates or enter tailing, waste waters, mine and natural drainage, and contribute to the formation of dust, which pollutes the atmosphere, soils, surface- and ground waters (Crane and Scott, 2012; Fu and Wang, 2011; Hudson-Edwards, 2003; Plathe et al.,

\* Corresponding author.

E-mail address: [yumikh@icct.ru](mailto:yumikh@icct.ru) (Y. Mikhlin).

2013; Wang et al., 2014). Aquatic (colloidal) nano- and micrometer-size particles transport various elements and substances in the environment in often larger quantities than dissolved species (Boyd, 2010; Gammons and Frandsen, 2001; Hochella et al., 2008; Hofacker et al., 2013; Hotze et al., 2010; Luther and Rickard, 2005; Rozan et al., 2000; Wang, 2014; Weber et al., 2009; Wigginton et al., 2007). The amount of ultrafine solids, including sulfides and oxides of toxic heavy metals derived from mineral industry, is expected to be much higher than, for instance, from emerging engineered nanomaterials, which presently attract considerable attention (Auffan et al., 2010; Cornelis et al., 2014; Garner and Keller, 2014; Mudunkotuwa and Grassian, 2011).

The formation of very fine-grained particulate material in the course of grinding of sulfide ores, and its fate in the environment require investigation in a variety of different ore types. In a recent study on Gorevskoe Pb-Zn sulfide ore (Mikhlin et al., 2016a), it was found that the yields of submicrometer particles and those less than 5 µm approach several tenths of vol.%, and a few vol.%, respectively. In this study, four samples from Cu-Ni and platinum group elements (PGE) bearing sulfide ores located at Krasnoyarsk territory in Siberia (Russia) were studied after drum milling. Three of them are the most important types of Noril'sk Deposits of Siberia (Dodin, 2002; Krivolutskaya, 2016); they comprise a high-grade Cu-Ni sulfide ore, disseminated low sulfide ore, and valleriite-rich "coppery" ore containing copper and sulfur largely as a layered metal sulfide/hydroxide mineral valleriite,  $4(\text{Cu,Fe}) \cdot 3(\text{Mg,Al})(\text{OH})_2$  (Evans and Allmann, 1968; Gubaidulina et al., 2007; Harris et al., 1970; Hughes et al., 1993; Laptev et al., 2009; Li and Cui, 1994). The disseminated ores of the lower portions of layered intrusions of gabbro-dolerite rock make up about 84% of total reserves at Noril'sk (several billion tons); Cu-rich, or "massive", sulfide ores (about 9% of the deposits) are located in metamorphosed rocks surrounding the intrusions; and the coppery ores (about 7% of the total reserves) form veins in sedimentary and metamorphic rocks on the margins of the massive ores. Valleriite-rich ore, however, has not typically been processed in the past due to technological problems (Laptev et al., 2009). A low sulfide Ni-Cu ore is from Kingash deposit located in Eastern Sayan; sulfides are mainly disseminated in the ultrabasic rocks, including metamorphized varieties (serpentinites) (Glazunov and Radomskaya, 2010; Lygin, 2010). Kingash ore cluster, the overall resources of which amount to 5.5 million tons of nickel and 2.3 million tons of copper (Lygin, 2010), is not in commercial exploitation till now, in part because of poor flotation performance that can be caused by gangue serpentine minerals (Algebraistova et al., 2012; Edwards et al., 1980; Feng et al., 2012, 2016; Kirjavainen and Heiskanen, 2007; Miettinen et al., 2010; Pietrobon et al., 1997; Senior and Thomas, 2005). The aim of the current research was to investigate granulometric distribution, composition, and surface characteristics of various fractions of the ground ores, with emphasis on potential effect of ultrafine particles, including colloids, on the technological processes and the environment.

## 2. Experimental study

### 2.1. Sulfide ore samples and preparation

Noril'sk Cu- and Ni-rich sulfide ore (Oktyabrskiy deposit) is composed of hexagonal pyrrhotite  $\text{Fe}_9\text{S}_{10}$ , and chalcopyrite ( $\text{CuFeS}_2$ ), cubanite ( $\text{CuFe}_2\text{S}_3$ ), and pentlandite  $[(\text{Ni,Fe})_9\text{S}_8]$ . The main elements are Fe (25–38 wt.%), S (25–30 wt.%), Cu (4–12 wt.%), Si (about 5 wt.%), with the content of Mg is as low as ~1%. The elemental compositions of representative samples of this and other ores determined using EDX analysis are given in Table 1 (see also Electronic Supplementary Information). The disseminated sulfide ore from Noril'sk-I deposit has much lower concentrations of sulfur (1–3 wt.%), iron (8–12 wt.%), heavy metals (Cu 2–3 wt.%, Ni 0.2–0.5 wt.%), whereas the amounts of Si, Al, and Mg approach 20 wt.%, 6–8 wt.%, and 7–10 wt.%, respectively. The sulfide minerals (pyrrhotite, chalcopyrite, pentlandite) are associated with gabbro dolerite rocks enriched with magnesian olivine and pyroxene (Grinenko, 1985; Krivolutskaya, 2016). Valleriite ore (Talnakh

**Table 1**

Surface concentrations (at.%) of main elements in the milled ores and their supernatant particles determined using XPS in comparison with EDX data.

	Fe	Cu	S	Si	Al	Mg	Ca	Cl	Ni	O
Noril'sk Cu-rich ore										
EDX	21.6	6.2	30.6	5.3	2.6	0.87	1.5	–	1.6	28.8
XPS	5.8	1.4	18.9	7.6	4.2	6.0	–	–	0.36	55.7
Supernatant particles	2.7	0.25	4.9	15.2	4.1	6.3	–	–	0.49	65.5
Noril'sk dissemin. ore										
EDX	4.4	0.76	0.88	15.5	5.6	9.7	2.4	–	0.2	59.3
XPS	1.8	tr.	tr.	19.9	6.2	11.6	0.90	–	–	59.2
Supernatant particles	1.3	0.24	tr.	19.8	4.6	10.3	0.81	–	–	58.2
Valleriite ore										
EDX	6.8	3.8	8.7	8.3	2.6	18.4	–	–	0.37	51.0
XPS	2.2	0.89	4.7	10.3	4.4	20.3	–	–	–	57.1
Supernatant particles	1.25	0.49	4.0	11.6	4.9	20.3	–	–	–	57.6
Kingash ore										
EDX	2.9	0.21	0.66	11.6	0.84	19.2	0.13	–	0.11	64.3
XPS	0.46	0.07	–	14.8	3.5	22.7	–	0.2	0.06	58.4
Supernatant particles	0.54	0.04	–	15.2	4.08	23.4	0.15	0.25	0.04	56.2

deposit) contains a large amount of sulfur (about 10 wt.%), iron (10–15%), copper and nickel (up to 10 wt.% and 1–2 wt.%, respectively), along with high Mg concentration (about 18 wt.%), and a lesser abundance of Si (up to 10%), and Al (below 3 wt.%). The content of valleriite is about 20%; the main other sulfide minerals are pyrite, chalcopyrite, pentlandite, and pyrrhotite. The ore samples also contain serpentine (largely lizardite  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ ), silicates, magnetite. Kingash ore from Upper Kingash deposit (average elemental concentrations, wt.%: Mg 22, Si 15, Al 1.1, Fe 7.6, Cu 0.6, Ni 0.3, S 1.0) is composed of up to 70–75% of serpentine minerals and iron and non-ferrous metals as magnetite (10–12%), chalcopyrite, pentlandite, and pyrrhotite (about 4% total). In all of the ores about 80% of non-ferrous metal is associated with sulfide.

The ore samples were crushed to less than 5 mm and ground in a laboratory drum mill with steel balls using solid/water/balls weight ratio of 1:0.4:9 or dry milled at the solid/balls ratio of 1:10. To prepare the slurries and colloidal particles, the ground ore samples were mixed in distilled water (10 wt.% solid) in a glass beaker for 5 min, and then allowed to sediment at room temperature ( $22 \pm 1$  °C) for a predetermined time, typically 40 min. Then a portion of the supernatant liquid was collected by a pipette at approximately 1 cm below the surface of the solution.

### 2.2. Electron microscopy and related techniques

The ground samples were characterized using scanning electron microscopy (SEM), backscattered electron imaging microanalysis (SEM-BSE), and energy dispersive X-ray analysis (EDX) utilizing a Hitachi TM 3000 instrument operated at acceleration voltage of 15 kV, equipped with a Bruker Quantax 70 EDX analyzer. Transmission electron microscopy images and selected area electron diffraction patterns (SAED) were acquired using a Hitachi S5000 microscope operated at accelerated voltage of 100 kV. Colloidal particles were prepared for TEM investigation by placing the supernatant droplet on a carbon coated copper grid and allowing it to dry at room temperature.

### 2.3. Laser diffraction, dynamic light scattering and zeta-potential measurement

Laser diffraction analysis with a Horiba LA-300 instrument was employed to determine granulometric composition of mineral particles down to 0.1 µm in aqueous slurries. Particle size and zeta-potential

Download English Version:

<https://daneshyari.com/en/article/4696777>

Download Persian Version:

<https://daneshyari.com/article/4696777>

[Daneshyari.com](https://daneshyari.com)