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BIO-BENEFICIATION OF MULTIMETAL BLACK SHALE ORE BY FLOTATION

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Within the framework of the EU co-funded Bioshale project the bio-benefication of multimetal black shale ore was studied. The EU-co-funded Bioshale project aims to define innovative biotechnological processes for ''eco-efficient'' exploitation of black shale ores. The ore sample was from the Talvivaara deposit in Finland. In the black shale ore sample, the total amount of sulphides was 31.5% of which the Ni-minerals pentlandite and altered pentlandite is 0.52%. Nickel is distributed into pyrrhotite and oxidized pyrrhotite, 32.5%, and pentlandite and altered pentlandite, 66.0%. Other sulphides are chalcopyrite (Cu), sphalerite (Zn), pyrite (Co) and alabandite (Mn). The ore sample contanied 12.3% graphite as a fine mixture with other minerals. In standard flotation, a low grade sulphide concentrate with 0.67 % Ni and nickel recovery of 74 % was obtained from the studied black shale ore. The mass of concentrate was then 34.5% of the ore feed. The recoveries of copper and zinc were 91%, of cobalt 89% and of manganese 53%. The content of carbon in the concentrate was 11.3% as graphite represents a naturally floating harmful mineral in the ore. The bioflotation tests showed that collector chemicals, i.e xanthates, had to be supplied to achieve reasonable flotation results. Out of the three tested bacterial strains, *Staphylococcus carnosus*, *Bacillus firmus* and *Bacillus subtilis*, the minor hydrophobic strain *S. carnosus* yielded the best test results. However, results of bioflotation tests failed to substantially improve the product recovery or grade.

Key words: black shale, flotation. biotechnology

INTRODUCTION

The increasing demand for metals and the decreasing availability of high-grade ores have led to numerous investigations to find better processing techniques and reagents to enable the development of low-grade deposits. Black shale ores can contain significant amounts of base metals, like the Talvivaara deposit in Finland is

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the largest known sulphide Ni-deposit_in Europe (Loukola-Ruskeeniemi and Heino, 1996). The EU-co-funded Bioshale project aims to define innovative biotechnological processes for ''eco-efficient'' exploitation of black shale ores. Biobeneficiation processes, i.e. bioflotation and bioflocculation, are generally very fast and have been extensively studied (Das et al., 1999; Santhiya et al., 2001; Sharma, 2001; Smith and Miettinen, 2006; Smith et al., 1993). The separation of minerals in bioflotation is governed by two major factors, the selective adhesion of microorganisms on mineral surface and the interaction of flotation chemicals with biologically pre-conditioned minerals (Sharma, 2001). The selective adhesion of microorganisms on minerals is required to modify the mineral surface properties for mineral separation either by flotation or flocculation.

This study aims to: (i) concentrate base metal containing sulphide minerals from multimetal black shale ore by flotation (beneficiation), (ii) improve the flotation by use of bacteria as activators or depressants (bio-beneficiation).

MATERIALS AND METHODS

PREPARATION OF ORE SAMPLE

An ore sample of 200 Mg (tons), -700 mm, was received from the Talvivaara black shale deposit. The sample was crushed to -80 mm (164 tons) and -12 mm (149 tons). The fine fraction was further crushed to -5 mm and subsequently -1 mm. The latter fraction was used in the bio-beneficiation tests.

CULTIVATION OF BACTERIA

The three bacterial strains *Staphylococcus carnosus*, *Bacillus firmus* and *Bacillus subtilis* were selected for bioflotation studies. The strains *S. carnosus*, *B. firmus* and *B. subtilis* were cultivated in shake bottles and pilot-fermenters (Table 1).

Table 1. Growth conditions and yields

Strain	Fermentation broth, Temperature 30°C				Cell suspension	
	Cultivation time (h)	pH	V (l)	Cell concentration (g d .w./l)	V (l)	Cell concentration (g d .w./l)
S. carnosus	18	>4.8	200	4.8	4	168
S. carnosus	19	>6.0	20	6.4	0.6	213.5
B. firmus	17	>6.8	200	1.9	2	63
B. subtilis	16	6.8	20	2.2	0.2	83
B. subtilis	16	>6.6	20	1.7	0.4	78

FLOTATION TESTS

For flotation tests, a subsample (1 kg) from the -1 mm fine fraction of black shale ore was ground in a stainless steel ball mill (8 kg balls) with 0.7 dm^3 water and water glass (500 g/t) for 45 min. The yielded particle size d80 was 78 µm. After grinding the slurry was placed in a 4-l flotation cell and water was added to make slurry density 25%. All experiments were carried out in Outokumpu cell (4 dm^3) with an air flow of 3 dm^3/min, stirring speed of 1800 rpm. Freeze dried bacterial cells were used (Table 1 and 2) and conditioned at ambient pH of 6.4-6.6 of tap water. In some of the tests the rougher concentrate (RC) was cleaned by successive 1 to 3 cleaning steps to yield a cleaner concentrate (CC). The chemicals used in the flotation tests are given in Table 3. An overview of the experimental set ups is given in Table 2.

Table 2. Experimental set up of bioflotation and reference flotation (19, 37, 39) tests (RC rougher concentrate, CC cleaner concentrate). Tests without addition of collectors are marked bold. Potassium Amyl Xanthate (KAX), Sodium Isobutyl Xanthate (NaIX)

Test		Bacterial strain (g/t)			Xanthate (g/t)		pH
		Staphylococcus carnosus	*Bacillus firmus*	*Bacillus subtilis*	KAX	NaIX	RC/CC
Bio-1	**RC**	**800**					**4**
Bio-2	RC	400			400		4
Bio-3	**RC**	**400**					**4**
Bio-4	RC	400			400		4
Bio-5	**RC**	**800**					**4**
Bio-6	**RC**	**800**					**4**
Bio-7	**RC**	**4000**					**4**
Bio-8	RC	400				150	10.5
Bio-10	**RC**	**800**					**4**
Bio-11	CC	3000			1300		4/5.6-7.7
Bio-12	RC	400				300	10.5
Bio-13	RC	400			300		10.5
Bio-14	RC		400		300		10.5
Bio-15	CC	1600			800		10.5/9.0-9.8
Bio-16	CC		1200		1300		4/5.7-7.6
Bio-17	RC			400	300		10.5
Bio-18	CC			1200	1300		4/5.6-7.3
Bio-19	CC	1200			1300		4/9-10
Bio-20	CC	1200			800		10.5/9.1-9.8
19	CC				750		4/6.2-6.4
37	CC				1300		4/5.9-8.3
39	CC				1300		4/5.2-6.8

Table 3. Chemicals applied in flotation tests

Chemical	Function
Water glass	Dispersant
Sulphuric acid	pH control
Calcium hydroxide	pH control
Copper sulphate	Activator for sulphide minerals
Potassium Amyl Xanthate (KAX)	Collector for sulphide minerals
Sodium Isobutyl Xanthate (NaIX)	Collector for sulphide minerals
Carboxy methyl cellulose (CMC)	Depressant for silicates and graphite
Polyglycol ether (Dow250)	Frother (froth stabilizer)

ANALYSES

The collected concentrates and tailing products of the tests were filtered, dried and weighed. The samples were separated for chemical analyses. The elements Ni, Cu, Co, Zn, Mn and Fe were analyzed with Atomic Absorption Spectroscopy after nitric acid dissolution. Sulphur and carbon were determined with combustion analysis using a Leco analyzer. In addition, X-ray fluorescence was used to determine content of 40 elements in the samples. The masses and analyses of flotation products were used to calculate the feed assay and the recoveries of main elements to flotation products.

The identification of minerals and the mineral composition of the Talvivaara ore sample were determined by using combined Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray analysis (EDAX) with the associated image analysis system of a Mineral Liberation Analysis equipment. The microprobe analyses of sulphide minerals were carried out with a Camexa SX 100 analyzer.

RESULTS AND DISCUSSION

In brief, the geochemical composition of the black shale ore sample was as shown in Table 4. The most abundant mineral group in the ore is formed by different silicates; i.e. quartz 16.7 %, biotite 12.0 % and plagioclase 10.3 %. The total amount of sulphides is 31.5 % of which the Ni-minerals pentlandite and altered pentlandite is 0.52% (Table 4). As much as 32.5 % of nickel is carried by pyrrhotite and 66.0% by Ni-minerals, i.e. pentlandite and altered pentlandite. Other sulphides are chalcopyrite (Cu), sphalerite (Zn) and alabandite (Mn). The ore contains 12.3 % graphite (as a fine mixture with other minerals), the chemical analysis of total carbon results in 7.72 % (Table 4).

The challenges in the beneficiation of this black shale ore are connected with the mineralogical characteristics of the ore. A high grade nickel concentrate cannot be produced with a good recovery because one third of nickel is contained by pyrrhotite. This means that in order to reach a good nickel recovery all sulphides must be recovered to concentrate whereby the grade remains low as the Ni-content of the sulphide phase is 0.845 % only.

Another challenge in the black shale ores is carbon which occurs in the form of graphite in the ore. As a soft mineral graphite forms easily fine slime particles in grinding and in addition to this, graphite is naturally floated without any reagents. Graphite was only partially depressed in flotation and formed one of the major harmful constituents in the concentrates.

The reference flotation tests with standard chemicals indicated that a concentrate containing 0.67 % Ni with a nickel recovery of 74 % was obtained by flotation (Test 39, see Table 5). The amount of concentrate was then 34.5 % of the mass of ore feed (Table 5). The flotation concentrate is a bulk concentrate of all sulphide minerals. The recoveries of copper, zinc and cobalt were about 90 % being thus higher than the recovery of nickel.

Table 4. Major geochemical and mineralogical composition of the black shale ore sample

Element		Chemical analysis		Microprobe analysis of sulphide minerals in total 31.5% of ore (% of element in mineral)						
		Initial	Corrected*	Pyrrhotite+ Oxidized pyrrhotite 19.83% of ore	Pyrite 7.76% of ore	Alabandite 1.79% of ore	Sphalerite 1.05% of ore	Chalcopyrite 0.50% of ore	Altered Pentlandite 0.47% of ore	Pentlandite 0.05% of ore
Ni	%	0.326	0.305	0.44	0.05	0	0.01	0.01	33.97	35.10
Cu	%	0.215	0.228	0	0	0	0	33.89	0	0
Zn	%	0.589	0.589	0.01	0	0.01	53.34	0.19	0	0.01
Co	%	0.033	0.033	0	0.39	0	0	0	1.04	0.83
Fe	%	13.12	13.12	52.46	46.67	3.24	7.52	30.58	20.31	30.02
Mn	%	1.23	0.913	7.46	0.01	58.47	4.14	0.02	0.01	0.07
S	%	13.0	11.0	39.10	52.78	36.43	33.72	34.81	41.67	33.33
C total	%	6.45	7.72							
Distribution of Ni between sulphide minerals (%)				**32.5**	**1.4**				**59.5**	**6.5**

*Average of feed analysis of 40 flotation tests

Table 5. Comparison of flotation products

	Product	Mass	Ni	Ni-recovery
Flotation		wt-%	%	%
Test 39	Rougher concentrate	65.7	0.436	91.8
	CC1	20.8	0.712	47.4
	CC2	25.8	0.729	60.2
	CC3	**34.5**	**0.672**	**74.3**
Bioflotation				
Test BIO-11	RouQher concentrate	72.6	0.390	93.6
	CC1	52.2	0.484	83.4
	CC2	**29.0**	**0.648**	**62.1**
	CC3	16.8	0.782	43.3
Test BIO-20	Rougher concentrate	64.6	0.451	85.4
	CC1	49.10	0.506	72.7
	CC2	42.00	0.539	66.2
	CC3	25.10	0.756	55.5

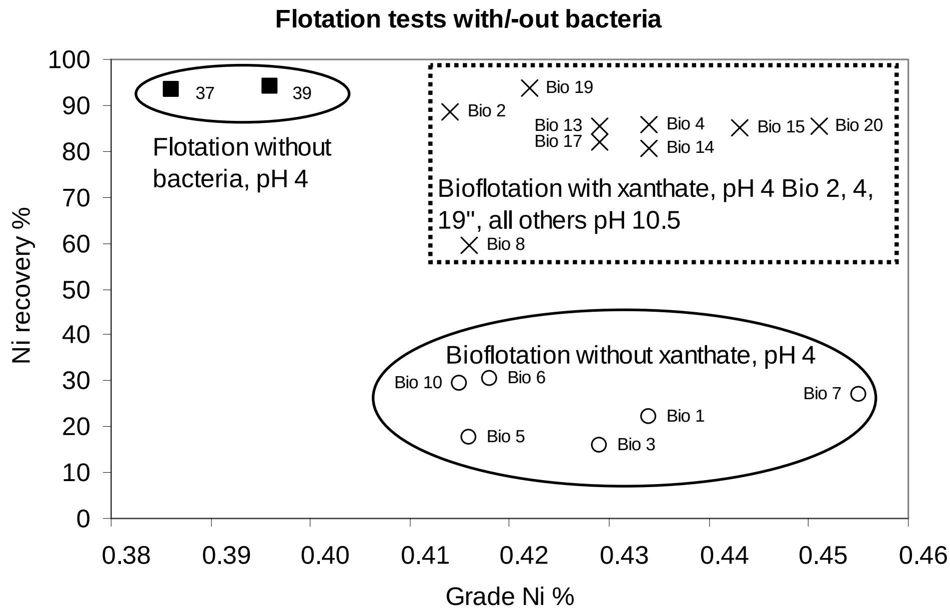

Fig. 1. Ni-recovery and grade in 2nd rougher concentrate during flotation.
Experimental conditions see Table 2

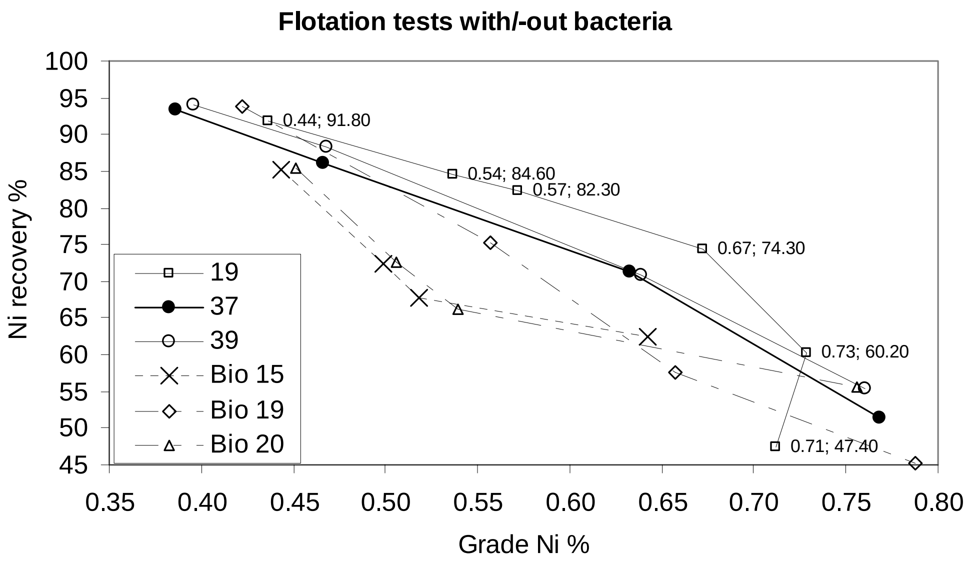

Fig. 2. Ni-recovery during cleaner flotation of black shale ore. Experimental conditions see Table 2

Table 6. Mineralogical composition of ore sample and bioflotation products

	Ore	BIO-11					BIO-15			
	Content (%)	Content (%)					Content (%)			
Mineral		T	CC3	CT3	Feed		T	CC3	CT3	Feed
Quartz	16.7	22.4	1.3	17.7	16.2		19.6	6.0	18.0	14.8
K_Feldspar	1.4	1.7	0.2	2.1	1.7		1.8	0.6	3.1	1.8
Plagioclase	10.3	10.2	0.9	19.2	13.6		10.8	5.6	21.9	12.7
Tremolite	4.1	5.9	0.2	5.5	4.7		7.4	0.9	6.6	5.1
Biotite	12.0	28.2	0.5	14.2	15.7		31.0	2.9	13.2	16.5
Chlorite	1.3	3.9	0.2	1.8	2.1		3.5	0.4	2.2	2.1
Apatite	1.0	1.4	0.1	2.1	1.6		1.6	0.7	2.5	1.6
Pyrrhotite	15.6	0.0	56.3	9.5	14.9		0.3	45.6	2.9	15.3
Pvrrhotite_altered	4.3	0.2	6.0	2.1	2.2		0.4	5.6	2.2	2.6
Pvrite	7.8	0.1	20.6	2.1	4.7		0.6	15.2	1.7	5.5
Chalcopyrite	0.5	0.0	3.9	0.3	0.8		0.0	2.0	0.5	0.8
Pentlandite	0.0	0.0	0.7	0.1	0.2		0.0	0.4	0.1	0.2
Pentlandite_altered	0.5	0.0	1.4	0.4	0.5		0.0	1.0	0.5	0.5
Sphalerite_**Mn**	1.0	0.0	3.9	0.5	0.9		0.0	2.7	0.5	1.0
Alabandite	1.8	0.0	0.7	2.1	1.3		0.3	2.4	0.7	1.1
Goethite	1.9	5.0	0.3	0.6	1.7		3.8	0.3	0.8	1.7
GraDhite+Minerals	12.3	18.2	1.6	15.6	13.9		15.6	5.2	18.2	13.2
Unknown	7.5	2.7	1.4	4.0	3.2		3.2	2.3	4.4	3.3
Total	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**		**100.0**	**100.0**	**100.0**	**100.0**

CONCLUSIONS

A low grade sulphide concentrate with 0.67 % Ni and nickel recovery of 74 % was floated from the studied black shale ore by using common flotation chemicals. The mass of concentrate was then 34.5% of the ore feed. The recoveries of copper and zinc were 91%, of cobalt 89% and of manganese 53%. The content of carbon in the concentrate was 11.3% as graphite represents a naturally floating harmful mineral in the ore.

The bioflotation tests showed that collector chemicals, i.e xanthates, had to be supplied to achieve reasonable flotation results. Out of the three tested bacterial strains, *Staphylococcus carnosus*, *Bacillus firmus* and *Bacillus subtilis*, the minor hydrophobic strain *S. carnosus* yielded the best test results. However, results of bioflotation tests failed to substantially improve the product recovery or grade.

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W ramach programu „BIOSHALE”, sponsorowanego przez Unię Europejską, badany był proces biowzbogacania polimineralnej rudy łupkowej. Celem projektu było opracowanie innowacyjnej metody eksploatacji rudy łupkowej w sposób przyjazny dla środowiska naturalnego. Ruda łupkowa pochodziła ze złoża Talvivaara zlokalizowanego w Finlandii. Próby rudy zawierały minerały siarczkowe, których całkowita zawartość wynosiła 31,5%. Nikiel znajdował się w pirotynie 32,5% i w pentlandycie 66.0%.

Inne siarczki jakie występują w rudzie to chalkopiryt (Cu), sfaleryt (Zn), pirotyn (Co) i alabandyt (Mn). Próba rudy zawierała grafit w formie mieszaniny drobnych ziaren z innymi minerałami. W procesie flotacji rudy otrzymywano koncentrat siarczkowy o zawartości 0,67% niklu z uzyskiem 74%.

Zagęszczenie nadawy na flotację wynosiło 34,5 %. Uzyski miedzi i cynku kształtowały się na poziomie 91% i 89%. Uzysk manganu wahał się na poziomie 53%. Zawartość węgla w koncentracie wynosiła 11,3%. Występował on w formie naturalnie flotującego grafitu. Próby bioflotacji pokazały, ze kolektor flotacyjny typu ksantogenian musi był zastosowany w celu uzyskania korzystnych wyników. Z trzech testowanych szczepów bakteryjnych: *Staphylococus carnosus, Bacillus firmus* i *Bacillus subtilis* najbardziej hydrofobowym szczepem okazał się być szczep *Staphylococus carnosus*, który dawał najlepsze wyniki flotacji. Jednakże, wyniki bioflotacji wskazują, że nie udało się w sposób istotny poprawić uzysk i wychód koncentratu flotacyjnego.

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Ni	%	0.326	0.305	0.44	0.05	0	0.01	0.01	33.97	35.10
Cu	%	0.215	0.228	0	0	0	0	33.89	0	0
Zn	%	0.589	0.589	0.01	0	0.01	53.34	0.19	0	0.01
Co	%	0.033	0.033	0	0.39	0	0	0	1.04	0.83
Fe	%	13.12	13.12	52.46	46.67	3.24	7.52	30.58	20.31	30.02
Mn	%	1.23	0.913	7.46	0.01	58.47	4.14	0.02	0.01	0.07
S	%	13.0	11.0	39.10	52.78	36.43	33.72	34.81	41.67	33.33
C total	%	6.45	7.72							
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*Average of feed analysis of 40 flotation tests