

SELECTIVE DISSOLUTION AND DETERMINATION OF SULPHIDES IN NICKEL ORES BY THE BROMINE-METHANOL METHOD

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Bromine-methanol dissolution, which is mainly used in analysis of metallurgical specimens, has been applied to geological samples. It has been established that a solution of bromine-methanol dissolves sulphides and arsenides very selectively but attacks silicates and oxides only slightly. An exception is pyrite, of which merely 7 to 8 % is dissolved under the conditions defined in the analytical instructions.

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Introduction

Economically, the most important nickel-bearing minerals in Finland are pentlandite, pyrrhotite, mackinawite, millerite, gersdorffite, niccolite, violarite and bravoite. In silicates the abundance of nickel is distinctly lower. Olivine, pyroxenes, amphiboles and micas, including serpentines, are the predominant silicates in this country in which nickel replaces isomorphically other metals. The concentration of nickel in olivine is comparatively high, averaging 1330 ppm (Häkli 1971) in Finnish peridotites. Pyroxenes and amphiboles are only slightly dissolved in

acids, unlike olivine and serpentine whose ready dissolution affects analytical results. In the evaluation of marginal deposits, but also in the context of some other research programmes, it is of importance that the abundance of sulphide nickel recoverable through concentration processes be properly determined. Thus it was essential to develop a method which allows the selective assaying of nickel from nickel ores in the presence of diverse silicate combinations.

In the literature, several selective dissolution methods are reported dealing with the determination of sulphides in the presence of silicates. Mention may be made of the bromi-

Table 1. Nickel dissolved from olivine in brominated water leach as a function of the sulphur content in the sample.

S %	Percentage of Ni dissolved from the total Ni in olivine
4	26
12	72
20	89
29	94

nated water leach (Czamanske and Ingamells 1970, Häkli 1971), the dissolution in brominated water and carbon tetrachloride (Karapetjan 1968), the use of hydrogen peroxide and ammonium citrate (Katsnelson and Osipova 1960), the hydrogen peroxide and ascorbic acid leach (Lynch 1971) and chlorinating roast (Moss *et al.* 1961 and 1967). All these methods have certain disadvantages. The chlorinating roast is slow and thus ill-suited to everyday practice. In the applications of methods by Czamanske, Häkli, Katsnelson and Lynch the acidity of the solution depends on the amount of sulphides present. The development of sulphuric acid in samples containing abundant sulphides may lead to

partial dissolution of silicates. The water solution of serpentine shows an alkaline reaction, and so the nickel primarily dissolved by bromine may precipitate and go undetected in the analyses. The drawback to method of Katsnelson is the vigorous reaction of some minerals during dissolution. These unfavourable effects are listed in Tables 2 and 4. Table 1 demonstrates the dissolution of olivine in brominated water from samples containing pyrite.

In our search for a suitable method for the selective dissolution of geological samples, we paid particular attention to the bromine-methanol method that Korakas (1962) used to leach sulphides, and Kraft and Fisher (1963) metallic iron from metallurgical products. Filippova *et al.* (1973) have studied the solubility of synthesized pyrrhotite, pentlandite, heazlewoodite and millerite in bromine-methanol and other solvents. Sen Gupta and Chowdhury (1974) applied bromine-methanol digestion to the determination by AAS of sulphide nickel and cobalt in chondritic meteorites in the presence of

Table 2. The dissolution of nickel in brominated water leach from ultramafic samples, and the pH in the solution.

Sample	Ni, ppm		$Ni_2/Ni_1 \times 100$	% S	pH
	1	2			
Serpentinite Vuonos	1960	483	25	0.35	6.0
Serpentinite Vuonos	2000	2080	104	1.2	2.6
Ni tailings Kylmäkoski mine	1620	1230	76	1.2	2.4
Peridofite Kotalahti mine	1300	15	1.2	0.13	7.1
Serpentinite Hitura mine	4390	3730	85	1.1	3.8
Serpentinite Outokumpu	508	6	1.2	0.09	7.0
Lateritic Ni ore Larymna, Greece	181000	319	0.2	0.08	5.7

1. total nickel; HNO₃, HF and HClO₄ used. 2. nickel dissolved in brominated water.

Table 3 Brominated water leach at constant pH. Sample 2000 mg, 2 ml bromine, 20 ml water at 70°C pH kept constant by means of titration automatics.

Sample	Leaching time	pH	Ni, %		Ni _{dis.} /Ni _{tot.} × 100	MgO, %		MgO _{dis.} /MgO _{tot.} × 100
			dis.	tot.		dis.	tot.	
Peridotite	60	4.0	0.028	0.13	22	0.85	28.4	3.0
Kotalahti mine	60	5.0	0.014	0.13	11	0.59	28.4	2.1
	60	6.0	0.006	0.13	4.6	0.50	28.4	1.8
	60	4.0	0.069	18.1	0.4	0.09	1.9	4.7
Lateritic Ni ore Larymna, Greece	60	5.0	0.030	18.1	0.2	0.06	1.9	3.2
	60	6.0	0.010	18.1	0.1	0.05	1.9	2.6
	60	4.0	0.15	0.22	68	4.1	35.4	12
Serpentinite Hitura mine	60	5.0	0.092	0.22	42	0.8	35.4	2.3
	60	6.0	0.047	0.22	21	1.8	35.4	5.1
	60	4.0	0.14	0.20	70	0.98	35.7	2.7
Serpentinite Vuonos	60	5.0	0.072	0.20	36	2.2	35.7	6.2
	60	6.0	0.053	0.20	27	0.67	35.7	1.9

coexisting metal and silicate-oxide phases. As far as we know, however, brominemethanol leach has not been applied to the analysis of geological samples, of which low grade ultramafic nickel mineralisations, in particular, constitute a difficult, yet interesting topic. For many nickel and copper minerals of nickel ores the behaviour during bromine-methanol treatment is not reported in literature.

Bromine-methanol dissolution

The dissolution was carried out as follows:

Add 80 ml methanol p.a. and 5 ml bromine into a 500 erlenmayer flask fitted with a glass

Table 4. The dissolution of serpentinite (Outokumpu) in the brominated water as a function of the concentration of H₂SO₄.

For the brominated water leach, 5 ml water, 0.5 ml bromine and 1-n sulphuric acid were used. After the leach, the solution was diluted to 100 ml.

mH ₂ SO ₄ , 1-n	pH	Ni _{dis.} /Ni _{tot.} × 100	MgO _{dis.} /MgO _{tot.} × 100
—	6.6	< 1	1.4
0.5	6.5	< 1	1.8
1.0	6.2	1	2.9
2.5	4.4	16	5.8
10.0	1.7	46	14

stopper. Stir until the bromine goes into solution. Cool to room temperature before starting dissolution, to prevent the stopper from opening during shaking. Weigh into the erlenmayer flask 1 g of sample pulverised to the fineness required by analysis. Shake gently for 1 hour in a shaker. Filter in a fume cupboard through a white-band filter by using filter paper mass. Wash residue and filter paper six times with methanol. Add 10 ml nitric acid to the filtrate and evaporate carefully to dryness. Add 1 ml conc. hydrochloric acid and evaporate to dryness. Subsequently, add 5 ml hydrochloric acid and a little water, and dissolve by applying heat. Cool and dilute to 100 ml in a volumetric flask. The metals are determined by AAS. It is not recommended to prepare a stock of bromine-methanol solution, since the dissolving of bromine liberates so much heat that the mixture may start to boil.

Leaching tests

The solubility of various minerals was tested by subjecting them to the bromine-methanol leach as described above. In addition to the common nickel minerals, the

copper minerals that are usually associated with nickel ores, as well as some sulphides, were also tested. The minerals were: pentlandite, $(\text{Fe, Ni})_9\text{S}_8$, pyrrhotite (crystal structure not determined), millerite NiS , gersdorffite $(\text{Ni, Co, Fe})\text{AsS}$, niccolite NiAs , violarite $(\text{Ni, Fe})_3\text{S}_4$, chalcopyrite, cubanite CuFe_2S_3 , pyrite arsenopyrite FeAsS and sphalerite. Most of the minerals were extracted without separation from heavily mineralised samples. Unfortunately, no suitable samples of bravoite were available. The violarite sample contained abundant pyrite, and the cubanite specimen chalcopyrite. In the leaching test, the percentage of metal dissolved was calculated on the basis of the concentration in the original sample, and in residue or solution, or both. The dissolution of nickel and copper was studied from violarite and cubanite, respectively. For violarite, the results were checked by submitting the residue to microscopic examination. Furthermore, the dissolution of nickel oxide, prepared from nickel acetate by

roasting, was tested. Finally, comparative leaching was performed by using methods by Häkli, Katsnelson and Lynch, in addition to that of bromine-methanol (Table 6). The residue of the bromine-methanol leach was studied microscopically and it was noted that, apart from some inclusions and pyrite grains, all the sulphides had gone into solution.

Discussion

In the leach of a 1 g sample in accordance with analytical instructions, pentlandite, pyrrhotite, millerite, niccolite, chalcopyrite, cubanite and sphalerite dissolved completely in bromine-methanol. The behaviour of pyrite, gersdorffite and arsenopyrite, as well as nickel oxide, none of which are readily soluble, are compiled in Table 5. To bring arsenopyrite and gersdorffite completely or nearly into solution the samples had to be shaken for 4 hours and the amount of gersdorffite reduced to 0.1–0.25 g. Pyrite

Table 5. Leaching of minerals not readily attacked by bromine-methanol.

Mineral	Weight of sample, g	Leaching time, h	Dissolved, in %			
			Cu	Ni	Co	Fe
NiO	1.0	1		0.1		
Pyrite	1.0	1				6.8
	0.5	1				8.1
	0.25	1				7.1
	0.125	1				7.5
	0.25	4				15.1
	0.125	4				12.8
Gersdorffite	1.0	1		71	57	66
	0.5	1		74	58	66
	0.25	2		84	70	77
	0.25	4	94	91	80	86
	0.125	1		78	63	86
	0.125	2	95	95	88	86
	0.125	4	94	94	95	88
Arsenopyrite	1.0	1				80
	0.5	1				87
	1.0	4				93
	0.25	4				102
	0.125	4				101

Table 6. Selective leach by different methods. Legend: 1. dissolved 2. dissolved/total $\times 100$
 Concentration: Ni ppm, Mg, Fe and S %/o. For the method of Katsnelson the determinations are by AAS.

Sample no.	Total analysis				Bromine-methanol				H ₂ O ₂ -citrate				H ₂ O ₂ -ascorbic acid				Bromine-water				
					Ni		Mg		Ni		Mg		Ni		Mg		Ni		Mg		
	Ni	Mg	Fe	S	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	pH
1 Serpentinite Vuonos	1940	22.8	5.5	1.3	1860	96	0.24	1.1	1350	70	1.1	4.8	1880	97	2.8	12	2010	104	3.3	14	2.3
2 Serpentinite Outokumpu	2190	24.4	4.9	0.50	1710	78	0.54	2.2	1170	53	1.9	7.8	1530	70	3.4	14	346	16	1.1	4.5	5.5
3 Peridotite Kotalahti mine	1300	18.8	8.8	0.25	343	26	0.092	0.5	195	15	1.6	8.5	489	38	3.2	17	13	1	0.42	2.2	6.3
4 Ni tailings Kylmäkoski mine	1610	13.8	10.2	1.4	967	60	0.047	0.3	863	54	0.23	1.7	1160	72	2.1	15	1230	76	2.0	14	2.2
5 Serpentinite Hitura mine	5550	22.8	11.7	1.3	4410	79	1.1	4.8	4050	73	1.8	7.9	3420	62	5.0	22	3370	61	3.8	17	4.2
6 Lateritic Ni ore Laryma, Greece	188000	1.2	5.3	0.10	278	0.1	0.039	3.3	1620	0.9	0.095	7.9	9470	5.0	0.10	8.3	9	0.005	0.24	20	6.9
7 Olivine	720	30.8	5.6		4	0.6	0.006	0.02	36	5	0.26	0.8	3	0.4	0.092	0.3					

turned out to be surprisingly difficult to dissolve. During the normal leach of 1 hour, only 7 or 8 % of the mineral goes into solution. Extended leach does not help materially. With the method of Katsnelson and Osipova, 75 to 90 % of the pyrite in a 1 g sample went into solution within 2 to 4 hours. In practice, nickel oxide is insoluble in bromine-methanol. The out-comes of different methods are compiled in Table 6. They show that, as far as nickel analyses are concerned, the results given by the bromine-methanol and Lynch's methods are closest to each other. The method of Katsnelson gave average abundances 25 % lower than those obtained by the bromine-methanol method. Brominated-water leach failed in cases where $\text{pH} > 6$. Less magnesium was dissolved in the bromine-methanol leach than in the methods employed by Katsnelson and Lynch. Nevertheless, some

magnesium went into solution, especially from serpentine and oxides.

The repeatability of the bromine-methanol method was studied by submitting two samples to 10 leaches each. The results were as follows:

Serpentine from Vuonos: The solution contained 0.299 % Mg, $\text{SD} = \pm 0.057$ coefficient of variation 19.1 % and 1850 ppm Ni, $\text{SD} = \pm 17.4$ ppm, coefficient of variation 0.95 %.

Serpentine from Outokumpu: The solution contained 0.583 % Mg, $\text{SD} = \pm 0.039$ %, coefficient of variation 6.69 % and 1730 ppm Ni, $\text{SD} = \pm 16.7$ ppm, coefficient of variation 0.96 %.

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