



Leaching of manganese deep ocean nodules in $\text{FeSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ solutions

H. Vu^{a,*}, J. Jandová^a, K. Lisá^a, F. Vranka^b

^aDepartment of Metals and Corrosion Engineering, Prague Institute of Chemical Technology, Prague, Czech Republic

^bInteroceanmetal, Joint Organization, ul. Cyryla i Metodęgo 9, Szczecin, Poland

Received 27 May 2004; received in revised form 10 September 2004; accepted 22 September 2004

Abstract

Studies have been carried out to determine maximum extraction efficiency of Co, Ni, Cu and Mn from manganese deep ocean nodules in $\text{FeSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ solutions and to maximise Co, Ni, Cu and Mn concentrations in the resulting leach liquors. The leaching parameters such as sulphuric acid concentration, liquid-to-solid ratio, temperature, time and grain size of nodules were varied to study their effect on metal extraction. The optimum conditions established were as follows: stoichiometric amount of FeSO_4 , 1.6-fold excess over stoichiometric amount of H_2SO_4 , 90 °C, l/s of 7:1, grain size $\leq 1000 \mu\text{m}$. Under these conditions, more than 85% of Co and 90% of Ni, Cu and Mn could be extracted within 30 min. The leach liquors contained approximately 146 mg Co/L, 1.63 g Ni/L, 1.69 g Cu/L and 30 g Mn/L.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Manganese deep ocean nodules; Leaching in $\text{FeSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$; Influence of variable parameters on Co, Ni, Cu and Mn extraction

1. Introduction

Ocean nodules are being recognized as a source of various metals such as Co, Ni, Cu and Mn. These metals are present in nodules as oxides or hydroxides. The major matrices for Mn and Fe are todorokite (buserite), $\delta\text{-MnO}_2$, goethite, maghemite or Mn-hematite, but it is noted that these com-

pounds are usually amorphous in nature. The presence of ferric manganite in nodules is due to the substitution of ferric ions by manganous ions in the manganous hydroxide layer. The knowledge of the mechanism by which trace elements are incorporated within nodules is very important for their recovery on a hydrometallurgical way. It was found that nickel and copper are mainly associated with manganese oxide phases and cobalt mostly with the iron phase, but possibly also with the manganese oxides. It has been suggested that the most stable species of these elements in the ocean environment are MnO_2 , Fe_2O_3 , CuO , Ni_3O_4 and

* Corresponding author. Tel.: +420 2 2435 5025; fax: +420 2 2431 1136.

E-mail address: Vun@vscht.cz (H. Vu).

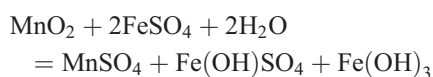
Co_2O_3 (Kotliński, 1999; Premchand and Jana, 1999; Brooke and Prosser, 1969; Fuerstenau and Han, 1983).

It is essential to reduce MnO_2 to promote its dissolution as well as dissolution of other metals associated with it. The various reducing agents used for the reduction of MnO_2 are SO_2 , FeSO_4 , charcoal and several others. The use of SO_2 as the reducing agent is preferred for its rapid rate of reaction, low temperature operation, ease of purifying leach liquor and elimination of barren solution disposal problem. Due to the high consumption of reducing agents required to dissolve the high quantity of MnO_2 , the use of SO_2 in place of others reducing agents can also decrease operational costs (Han and Fuerstenau, 1986; Acharya et al., 1999; Hancock and Fray, 1986).

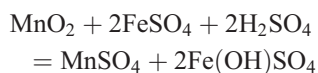
On the negative side, SO_2 is toxic, its utilization in industry is inconvenient both for its ecological and industrial hygiene aspects. Leaching the nodules in $\text{FeSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ solutions also provides rapid and efficient extraction of Co, Cu, Ni and Mn. Moreover, in contrast to leaching with SO_2 , this method of nodules processing does not bring any ecological risk. In addition, $\text{FeSO}_4\text{--H}_2\text{SO}_4$ solutions are available as waste pickling liquors or solid FeSO_4 , being the side product of TiO_2 manufacturing from ilmenite.

Treatment of manganic ore with acidified ferrous sulphate or pickle liquors (Das et al., 1982) was first reported in 1947. The reactions of manganese dioxide with ferrous sulphate solution can take place in three ways:

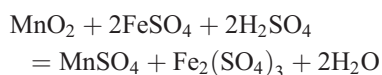
- (1) with neutral ferrous sulphate solution



- (2) with ferrous sulphate solution and small quantities of acid



- (3) with ferrous sulphate solution and excess acid



Investigation on acid leaching of manganese nodules have been carried out by numerous investigators (Brooke and Prosser, 1969; Fuerstenau and Han, 1983; Han and Fuerstenau, 1986). Fig. 1 presents an Eh–pH diagram for five major metals in nodules for a metal ion activity of unity at 25 °C. It is obvious from the figure that the advantage of acid leaching is in its selectivity. Copper is expected to be readily soluble from cupric oxide, while other oxides are not. If the Eh–pH conditions fall into Region A of Fig. 1, then nickel, copper and cobalt can be leached selectively from manganese and iron. By adjusting pH and Eh so that conditions depicted by Region B in the figure are achieved, it should be possible to dissolve manganese oxides and other oxides but iron oxides. By lowering the pH into Region C, conditions would exist where all five of the oxides should dissolve in the leach liquor.

The aim of this laboratory study was to determine optimum leaching conditions of manganese deep ocean nodules in $\text{FeSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ solutions to maximise extraction efficiency and concentration of valuable metals in leach liquors, especially of Co, Ni and Cu. Various process parameters, including quantity of H_2SO_4 in leach solutions, liquid-to-solid ratio (l/s), temperature, leaching time and particle size were studied.

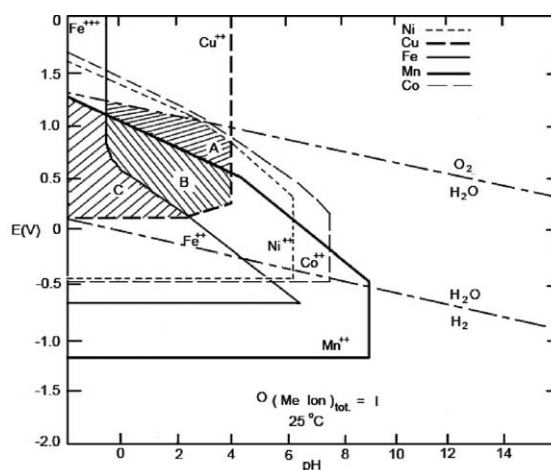


Fig. 1. Eh–pH diagrams for the Fe– H_2O , Mn– H_2O , Cu– H_2O , Ni– H_2O and Co– H_2O systems at 25 °C, unit activity (Han and Fuerstenau, 1986).

2. Experimental

2.1. Materials

In this study, leaching experiments were performed with manganese deep ocean nodules originating from the IOM area, located in the Clarion–Clipperton ore field. These nodules were mined in July 2001 during an expedition organized and sponsored by IOM, joint organization, Szczecin. Nodules were ground, sieved and the sample $\leq 1000 \mu\text{m}$ with specific surface of $108 \text{ m}^2/\text{g}$ or sample $\leq 180 \mu\text{m}$ with specific surface of $104 \text{ m}^2/\text{g}$ was used for experiments. Content of valuable metals in the nodules, Table 1, was determined after their decomposition by alkaline fusion by AAS method. Leach solutions were prepared from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and H_2SO_4 (Penta, analytical grade).

2.2. Procedure and equipment

Leaching experiments were carried out in a 2 L glass reactor fitted with a condenser and a thermometer, heated with a mantle controlled by a regulator and agitated with a mechanical stirrer. Depending on l/s ratio, the amount of nodules processed in each experiment varied from 100 to 200 g. To determine the time dependencies of dissolution of valuable metals, two regimes of leaching were conducted. Conditions of regime (1), under which the prevailing number of leaching experiments was conducted were as follows: a weighted amount of nodules was introduced in the reactor together with leach solution. The suspension was stirred, heated up to 80 or 90 °C and held at this temperature for 3 h. The l/s ratio ranged over 5:1, 7:1, 10:1 and 15:1. Samples of treated solutions (~20 mL) were periodically withdrawn, filtered and the filtrates were subjected to AAS analysis. The first sample was taken out when the reaction temperature reached the selected value (80 or 90 °C). In some cases as to eliminate the influence of

withdrawn samples on the extraction efficiency during leaching, the experiments were carried out without sampling. The metal extraction efficiency was determined from the composition of leach liquors at the end of leaching, the duration of which was 3 h. Conditions of regime (2) were established based on the results of leaching nodules according to regime (1) and were as follows: the acidic ferrous sulphate solution was introduced in the reactor and preheated to 90 °C. After reaching 90 °C, a weighted amount of nodules was added to the liquid while stirring. The liquid-to-solid ratio ranged over 7:1, 10:1 and 15:1.

In agreement with the results of our previous study (Jandová et al., 2003), the amount of FeSO_4 in all prepared solutions was stoichiometrically related to the amount required for MnO_2 reduction according to reaction (3). The quantity of sulphuric acid used varied from 1.2 to 1.8-fold excess over stoichiometric amount required for dissolution of all metals of interest, such as Co, Cu, Ni, Mn and Fe. Most leaching experiments were conducted with nodules fraction $\leq 1000 \mu\text{m}$. After completion of leaching, the leach residues were filtered, washed, dried, weighted and examined by XRF and XRD analysis.

3. Results and discussion

Results of nodule leaching in the $\text{FeSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ solutions according to regime (1) are shown in Fig. 2 as time dependencies of the extraction yield of Co, Ni, Cu and Mn.

Leaching of the nodules was performed with nodule fraction $\leq 1000 \mu\text{m}$ or $\leq 180 \mu\text{m}$, at temperatures of 80 or 90 °C. Reaction time was 3 h. Leaching was conducted in relatively dilute solutions, at l/s of 15:1, to eliminate the influence of the slurry on metal extraction. The quantity of FeSO_4 in leach solutions similar to all other leach solutions used in this study corresponded to the stoichiometric amount of FeSO_4 related to the reduction of Mn(IV) to Mn(II). At the same time, the quantity of H_2SO_4 corresponded to the 1.8-fold excess over stoichiometric amount of H_2SO_4 related to the dissolution of Co, Cu, Ni, Mn and Fe. In fact, the amount of FeSO_4 slightly exceeded the real stoichiometric amount of FeSO_4 necessary for the reduction of manganese oxides contained in the nodules because a part of manganese

Table 1
Content of valuable metals in dry residue of nodules

Fraction	Content [%]					
	Co	Cu	Ni	Zn	Mn	Fe
$\leq 1000 \mu\text{m}$	0.128	1.21	1.23	0.12	27.07	4.12
$\leq 180 \mu\text{m}$	0.123	1.30	1.25	0.137	27.34	4.03

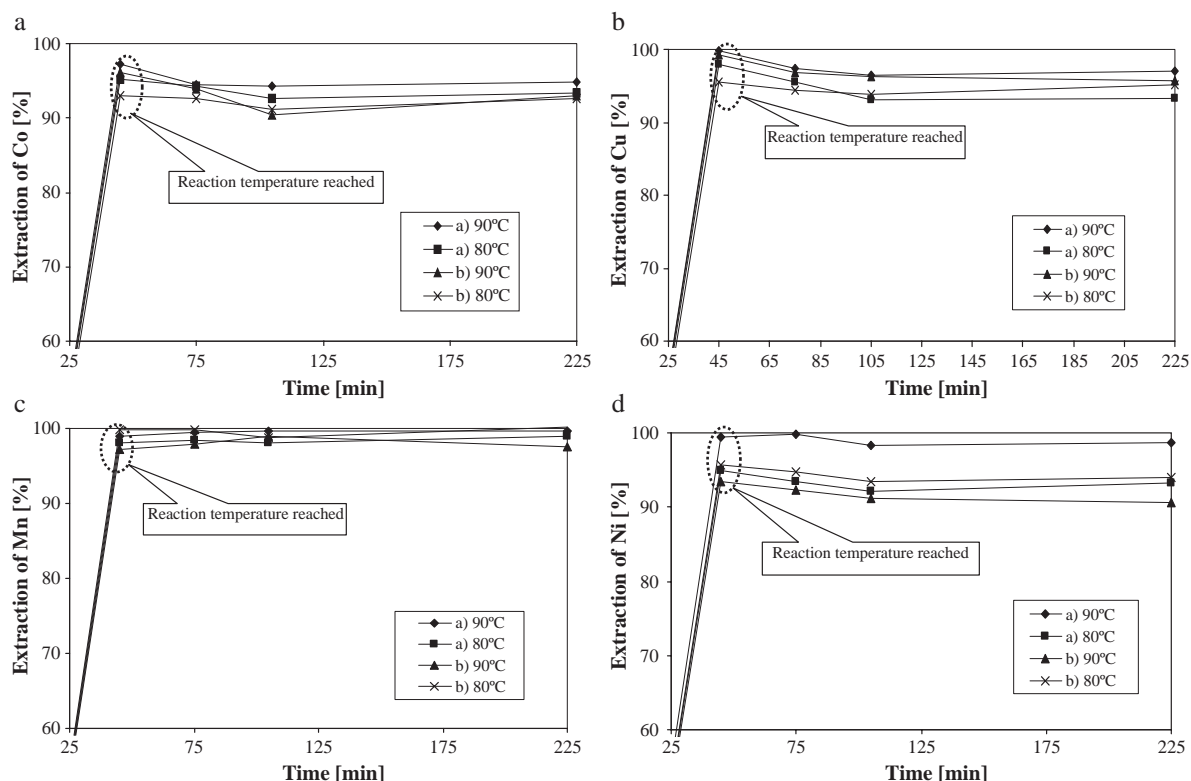


Fig. 2. (a–d) Kinetics of Co, Ni, Cu and Mn dissolution from manganese deep ocean nodules in solutions of stoichiometric amount of FeSO_4 , 1.8-fold excess over stoichiometric amount of H_2SO_4 , $l/s=15:1$, at 80 °C and/or 90 °C, (a) fraction $\leq 180 \mu\text{m}$, (b) fraction $\leq 1000 \mu\text{m}$.

is present as Mn(III) or even as Mn(II). However, on the basis of our preliminary studies (Jandová et al., 2003) and according to the literature (Brooke and Prosser, 1969), it is necessary to use leach solutions containing a slight excess of the precise stoichiometric amount of FeSO_4 to reach the maximum possible extraction efficiency of valuable metals. Using higher excess of FeSO_4 did not result in a significant increase in extraction efficiency (Premchand and Jana, 1999). According to our study (Jandová et al., 2003), the 1.8-

fold excess over stoichiometric amount of H_2SO_4 appeared to be sufficient to reach the maximum possible metal extraction.

From the results achieved it is obvious that dissolution of all metals of interest was completed almost immediately after reaching the desired temperature and that there were no differences between metal dissolution from the nodules fraction $\leq 1000 \mu\text{m}$ and fraction $\leq 180 \mu\text{m}$. This fact can be explained by the practically equal values of specific

Table 2

Results of leaching nodules in $\text{FeSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ solutions, $l/s=15:1$, 3 h, fraction $\leq 1000 \mu\text{m}$

Excess of H_2SO_4 [%]	Final pH	Metal concentration [mg/L]				Extraction efficiency [%]				Weight of leach residue [g]
		Co	Cu	Ni	Mn ^a	Co	Cu	Ni	Mn	
20	0.76	75	849	849	17.6	87	96	93	97	49.1
40	0.55	76	802	802	16.3	89	96	93	98	28.3
60	0.40	79	818	818	16.9	89	95	93	98	21.2
80	0.31	75	813	813	15.9	88	97	95	98	15.6

^a g/L.

Table 3
Results of leaching nodules in FeSO₄–H₂SO₄–H₂O solutions, l/s=10:1, 3 h, fraction ≤1000 μm

Excess of H ₂ SO ₄ [%]	Final pH	Metal concentration [mg/L]				Extraction efficiency [%]				Weight of leach residue [g]
		Co	Cu	Ni	Mn ^a	Co	Cu	Ni	Mn	
20	0.26	97	1621	1303	28.5	74	97	98	99	35.4
40	0.06	96	1649	1226	26.6	75	97	99	96	23.2
60	–0.15	108	1635	1246	22.6	85	98	99	97	16.7
80	–0.28	107	1603	1242	21.1	86	99	99	96	16.5

^a g/L.

surfaces of both fractions. It is also evident that leaching of nodules under the applied conditions provided very high extraction of all valuable metals. It is noted that extraction efficiency of all metals reached at 90 °C was slightly higher than that reached at 80 °C. For this reason, all further leaching tests were done at 90 °C.

The goal of the subsequent leaching experiments was to determine the lowest limit of H₂SO₄ concentration in leach solutions and possible lowering of l/s, which would ensure formation of leach liquors suitable for subsequent economical processing. Results of these experiments, which were performed according to regime (1) are summarised in Tables 2–5. Concentrations of Co, Cu, Ni and Mn and their extraction efficiencies at the end of 3 h leaching are also listed, having been performed with various excesses of H₂SO₄ and l/s ranging from 15:1 to 5:1. Chemical and mineralogical composition of selected leach residues is given in Table 6.

From the results achieved it is evident that the highest extraction efficiency of all valuable metals was achieved at l/s of 15:1, virtually irrespective of the amount of H₂SO₄ in leach solutions. However, leaching nodules in solutions containing lower H₂SO₄ concentrations led to the formation of larger amounts of leach residues due to the formation of jarosite, which is classified as a hazardous waste. It

is very probable that due to the tight environmental regulations in the European Union, disposal of jarosite containing wastes will not be acceptable solution in the near future (Kanari et al., 2002). Leaching of nodules at l/s of 10:1 or even at l/s of 7:1 provided comparable extraction efficiency with that obtained at 15:1 if leaching was performed in solutions containing at least 60% excess of stoichiometric amount of H₂SO₄. Under these conditions, relatively small amounts of leach residues not containing any jarosite, were formed. However, in contrast to the extent of cobalt extraction, the dissolution of Cu, Ni and Zn was not influenced by the H₂SO₄ concentration in leach solutions. Lowering the l/s ratio to 5:1 resulted in significant decrease of cobalt extraction efficiency, while extraction efficiencies of other valuable metals remained practically the same. From the results achieved it can be concluded that the optimum leaching conditions for industrial processing of nodules should comprise leaching in solutions with 1.6-fold excess H₂SO₄, l/s of 7:1 and at 90 °C. Such conditions provided relatively high concentration of valuable metals in leach liquors simultaneously with relatively high extraction efficiency.

Optimum leaching time was determined from the kinetic measurements of nodules leaching, which was performed according to regime (2) under the follow-

Table 4
Results of leaching nodules in FeSO₄–H₂SO₄–H₂O solutions, l/s=7:1, 3h, fraction ≤1000 μm

Excess of H ₂ SO ₄ [%]	Final pH	Metal concentration [mg/L]				Extraction efficiency [%]				Weight of leach residue [g]
		Co	Cu	Ni	Mn ^a	Co	Cu	Ni	Mn	
20	0.14	134	1621	1680	35.9	76	96	98	95	32.2
40	–0.18	138	1649	1705	36.1	80	97	99	96	19.9
60	–0.39	146	1635	1690	30.0	87	99	99	92	18.3
80	–0.55	146	1603	1678	28.5	86	97	99	95	18.0

^a g/L.

Table 5

Results of leaching nodules in $\text{FeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ solutions, $l/s=5:1$, 3 h, fraction $\leq 1000 \mu\text{m}$

Excess of H_2SO_4 [%]	Final pH	Metal concentration [mg/L]				Extraction efficiency [%]				Weight of leach residue [g]
		Co	Cu	Ni	Mn ^a	Co	Cu	Ni	Mn	
20	0.13	205	2163	2167	45.0	70	94	92	95	31.0
40	-0.60	177	2315	2387	52.1	71	94	95	96	18.6
60	-0.88	183	2301	2397	49.9	77	95	97	92	19.4
80	-0.95	187	2208	2313	46.0	79	96	99	95	17.8

^a g/L.

Table 6

Chemical composition of selected leach residues after 3 h leaching, fraction $\leq 1000 \mu\text{m}$

Leaching conditions		Elemental content [%]										
l/s ratio	Excess of H_2SO_4 [%]	Co, Ni, Cu	Mn	Fe	Si	Al	Ca	Mg	Na	K	Ti	S
10:1	80	<0.01	0.02	1.52	32.9	6.79	1.31	0.47	1.14	1.70	0.32	1.32
	60	<0.01	0.04	2.71	30.9	7.13	1.67	0.61	1.06	1.78	0.36	1.59
	40	<0.01	0.10	13.46	21.0	5.42	0.91	0.59	0.96	3.17	0.36	5.50
7:1	80	<0.01	0.03	0.99	33.1	6.10	2.08	0.36	1.05	1.54	0.28	1.77
	60	<0.01	0.05	1.49	31.5	6.32	2.66	0.44	1.05	1.56	0.30	2.32
	40	<0.01	0.10	6.06	27.9	6.40	1.62	0.60	1.05	2.26	0.35	3.04
5:1	80	<0.01	0.07	0.69	30.5	5.21	4.22	0.27	1.01	1.36	0.24	4.07
	60	<0.01	0.23	0.97	29.2	5.17	4.81	0.28	0.96	1.35	0.24	4.85
	40	<0.01	0.03	1.18	28.5	5.51	5.07	0.36	0.91	1.38	0.26	4.78

ing conditions: 1.6-fold excess over H_2SO_4 , l/s ranging over 7:1, 10:1 and 15:1, at 90°C , 3 h. It was evident that dissolution of all metals of interest proceeded extremely fast and it was completed within 30 min. However, in fact the time dependencies obtained are not established at a precise constant temperature due to the exothermic reaction of the

nodules with the leach solution, resulting in a temporary temperature increase of the reaction mixture. The typical kinetic dependency of valuable metal dissolution at l/s of 10:1 is illustrated in Fig. 3.

4. Conclusions

Leaching of nodules in $\text{FeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ solutions proceeds very rapidly and it is completed immediately after reaching the reaction temperature if the nodules are introduced in the reactor together with the leach solution at the laboratory temperature.

More than 90% of Ni, Cu and Mn can be extracted by leaching the nodules in solutions containing stoichiometric amount of FeSO_4 irrespective of the excess over stoichiometric amount of H_2SO_4 at 90°C under l/s varying from 5:1 to 15:1.

More than 85% of Co can be extracted at 90°C in solutions containing stoichiometric amount of FeSO_4 and at least 1.6-fold excess over stoichiometric amount of H_2SO_4 if the l/s ratio varied from 7:1 to 15:1. Lowering the l/s ratio resulted in decreasing the cobalt extraction efficiency below 80%.

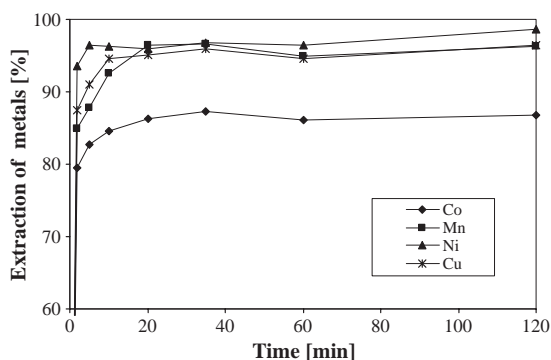


Fig. 3. Kinetics of Co, Ni, Cu and Mn dissolution from manganese deep ocean nodules in solutions of stoichiometric amount of FeSO_4 , 1.6-fold excess over stoichiometric amount of H_2SO_4 , $l/s=10:1$, at 90°C .

Lowering the reaction temperature caused a decrease of the extraction yield of all metals of interest.

The optimum conditions of nodules leaching in $\text{FeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ solutions are as follows: stoichiometric amount of FeSO_4 , 1.6-fold excess over stoichiometric amount of H_2SO_4 , 90 °C and l/s of 7:1. Resulting leach liquors contained approximately 146 mg Co/L, 1.63 g Ni/L, 1.69 g Cu/L and 30 g Mn/L.

Acknowledgement

The work was supported by the Interoceanmetal, Joint Organization, Szczecin, Poland and by the Research intention MSM No. 223100002.

References

- Acharya, R., Ghosh, M.K., Anand, S., Das, R.P., 1999. Leaching of metals from Indian ocean nodules in $\text{SO}_2\text{-H}_2\text{O-H}_2\text{SO}_4\text{-NH}_4\text{SO}_4$ medium. *Hydrometallurgy* 53, 169–175.
- Brooke, J.N., Prosser, A.P., 1969. Manganese nodule as a source of copper and nickel—mineralogical assessment and extraction. *Trans. Inst. Min. Metall.* 78, 64–67.
- Das, S.C., Sahoo, P.K., Rao, P.K., 1982. Extraction of manganese from low-grade manganese ores by FeSO_4 leaching. *Hydrometallurgy* 8, 35–47.
- Fuerstenau, D.W., Han, K.N., 1983. Metallurgy and processing of marine manganese nodules. *Miner. Process. Technol. Rev.* 1, 1–83.
- Han, K.N., Fuerstenau, D.W., 1986. Extraction behaviour of metallic elements from deep sea manganese nodules in reducing medium. *Mar. Min.* 2, 155–169.
- Hancock, H.A., Fray, D.J., 1986. Use of coal and lignite to dissolve manganese dioxide in acidic solutions. *Trans. Inst. Min. Metall.* 95, 27–34.
- Jandová, J., Hong, V., Lisá, K., Selucká, J., 2003. Processing of manganese deep ocean nodules. Research Report sponsored by IOM Szczecin, Prague, Czech Republic.
- Kanari, N., Bonayebi, A., Allain, E., Gaballah, I., 2002. Decontamination of jarosite through thermal treatment. In: Bjorkman, B., Samuelsson, C., Wikstrom, J.O. (Eds.), *Recycling and Waste Treatment in Mineral and Metal Processing: Technical and Economical Aspects*, Proceedings of TMS Fall 2002 Extraction and Processing Division Meeting, TMS, vol. 2. Lulea, Sweden, pp. 953–958.
- Kotliński, R., 1999. Metallogenesis of the world's ocean against the background of ocean crust evolution. *Special Papers*, vol. 4. Polish Geological Institute, Warszawa, pp. 1–59.
- Premchand, J.R., Jana, R.K., 1999. Processing of polymetallic sea nodules: an overview. In: Jin, S.C., Rahul, S. (Eds.), *Proceedings of the Third (1999) ISOPE Ocean Mining Symposium*, Goa, India, pp. 237–245.