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LABORATORY TOOL FOR ELECTROCHEMICAL STUDY OF SULPHIDE MINERALS

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Sulphide mineral dissolution in aqueous media occurs by different mechanisms. The rate of the overall reaction is controlled by the rate of the slowest reaction step. Most important factor in the anodic dissolution of mineral sulphides is the formation of a reaction product layer, which affects the mass transfer rate, often the rate determining step of the overall reaction. In this work we have used electrochemical tests for evaluating factors affecting sulphide mineral dissolution. As an essential tool, an electrochemical measurement method for leaching behaviour of sulphide minerals has been developed. Development of a graphite paste electrode (GPE) for the electrochemical measurements has made it possible to investigate powdered sulphide mineral samples. This ensures that the measurement conditions are as close as possible to the real leaching conditions. The graphite paste electrode makes it possible to run electrochemical measurements reproducibly and reliably.

Key words: *sulphide mineral, dissolution, graphite paste electrode, electrochemical measurement*

INTRODUCTION

Measurements were conducted with samples prepared from minerals usually being in solid phase and having a low current resistance. Using of a graphite paste electrode (GPE) for the electrochemical measurements has made it possible to investigate powdered sulphide mineral samples. This ensures that the measurement conditions are as close as possible to the real leaching conditions. The aim of our study was to examine the to use GPE in electrochemical study of sulphide minerals. Special attention was paid on the differences at reaction rates between solid and graphite paste electrodes.

Carbon is available in several forms: amorphous, powder, graphite rods, and diamond. Carbonaceous materials have several properties that have attracted their use in electrodes: good electrical conductivity, acceptable corrosion resistance, availability in high purity, low cost, high thermal conductivity, dimensional and mechanical

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stability, light in weight and ease of handling, availability in a variety of physical structures and ease of fabrication into composite structures (Kinoshita 2001). The high conductivity of graphite and its good chemical stability are attractive features for its use in electrochemistry.

The first user of carbon powder as paste electrode was Adams and his research group probably in the fifties. The title of carbon paste electrode was mentioned first time in a scientific communication on Analytical Chemistry in 1958 (Adams 1958). In this study powder of graphite was used and the title of graphite paste electrode invented. Graphite paste electrodes have proved to be practically inert in the electrochemical measurements and thereby do not disturb the electrochemical reactions on the powder samples (Ahlberg et al. 1993), (Gerlach et al. 1983), (Rice et al.1983).

EXPERIMENTAL

The measurements were carried out using two electrochemical workstations: (1) a PAR 273 Potentiostat/Galvanostat controlled by EG&G PAR Model 352 Corrosion Analysis Software 1.00 and (2) Potentiostat/Galvanostat 2000 working together with NF Electronic Instruments 5050 frequency response analyzer (FRA) and NF Electronic instruments 1731 Intelligent/Arbitrary function synthesizer controlled by in-house written software.

A three-electrode AVESTA type electrochemical cell was used for the electrochemical measurements (Figure 1). The cell contained a working electrode, a reference electrode and an auxiliary platinum electrode. To adjust the temperatures between 23-83 ˚C the cell was thermostatted. In all the measurements the cell was stirred with a mechanical stirrer at 500 rpm.

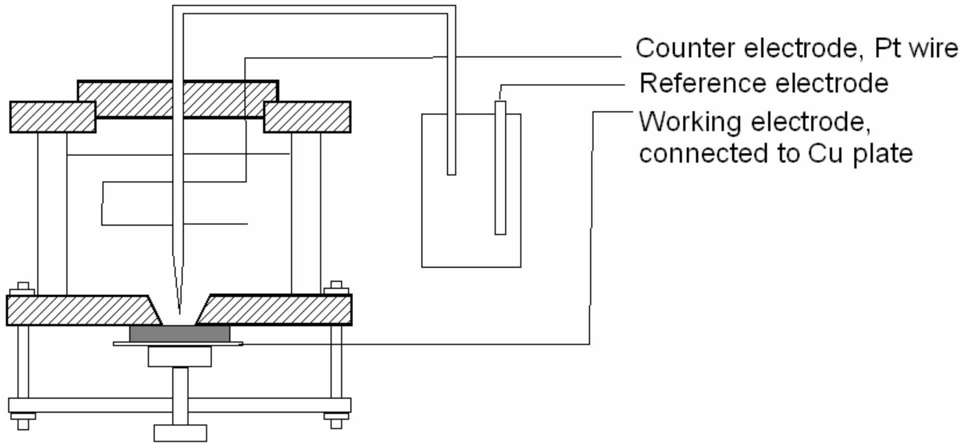

Fig. 1. Simplified diagram of the Avesta cell

The reference electrode used was Hg/Hg_2Cl_2 filled with saturated KCl (trademark: Radiometer analytical, REF 421). The reference electrode was situated in a glass tube (145 mm high, Ø11 mm, Schott Geräte B522), which was filled with a saturated KCl, and KCl salt. On the bottom of the tube there was a platinum gauze. The reference electrode in the glass tube was positioned in an external beaker and connected to the cell with a Haber-Luggin capillary. The composition and the pH of the solution in the beaker were the same as in the cell, but the temperature could not be increased (Figure 2). In consequence of this, the temperature in the beaker was between 21-24 ˚C during the measurements.

Fig. 2. Modified Avesta cell used in solid sample leaching experiments

The solution used in the electrochemical tests was a saturated solution of calcium sulphate. The solution was made by adding a constant amount (2.41 g) of $CaSO_4$ into a dm^3 of distilled water. The use of calcium salt was to provide hardness salts to the solution to increase conductivity. The temperature and the pH values of the solution were adjusted in each measurement. The temperature was varied between 23 and 83 ˚C. The pH was monitored in the range of 0.5 to 3.5. The upper pH limit is defined by the formation of ferrous hydroxide, while the lower limit is due to the bacteria activity.

The black shale mineral came from the Talvivaara mine, Finland. The mineral sample was non-homogenous and the composition varied. Solid electrodes were made for the electrochemical measurements. Figure 3. shows a photograph of electrodes.

A set of working electrodes of black shale was made. The most uniform pieces (visually) of the black shale (30x20x20 mm) were chosen (a mineral rich area) and were cut with a diamond cutter. The conductivity of the electrode was tested and it was checked that the resistance of the electrode was 2-5 Ω. The polishing of electrodes was carried out between every measurement with rotating and wetted abrasive paper. The waterproof abrasive paper used was of grade 800 mesh. The uniformity was inspected visually. After polishing the electrodes were rinsed first with deionised water and ethanol (ETAX Aa, 99.5% ethanol) and then dried with a hairdryer. Some chemical analyses of Talvivaara ore are shown in Table 1.

Fig. 3. Prepared black shale working electrodes with mineral rich area.

The black shale materials contain significant amount of carbonaceous material. Therefore it was decided not to use a former construction of graphite paste electrode (Forsén et. al. 1996). Instead the graphite was mixed with the test material and put in a special holder. The holder was necessary to avoid sample disintegration due to gas evolution. The best graphite paste electrode construction was made by using a mixture of graphite powder (Merck KGaA, Germany, bulk density 20-30 g/100ml), powder samples of Talvivaara black-shale ore, size 1 mm and paraffin oil, Figure 4.

Table 1. Talvivaara black shale analyses

	Fe, ppm	Ni, ppm	Cu, ppm	Zn, ppm	Mn, ppm	Co, ppm	Reference
Black shales Ni < 0,1%	88000	500	600	2600	1600		(Loukola-Ruskeeniemi et. al. 1999)
Black shales Ni ≥ 0,1%	104000	2600	1300	5200	2600		(Loukola-Ruskeeniemi et. al. 1999)
Black schist ore	158000	2800	1400	3900	2900	200	(Riekkola-Vanhanen et. al. 2001)
Bioshale sample	118767	2494	1514	5157	5672	260	(www.talvivaara.com)

Fig. 4. Construction of the graphite paste electrode

RESULTS AND DISCUSSION

POLARISATION CURVES FOR TALVIVAARA ORE

The usability of graphite paste was verified by comparing polarization curves of solid sample to that of powdered sample, Figure 5. The polarization curves of solid and powder samples are close to each other whereas the graphite materials have much lower current densities.

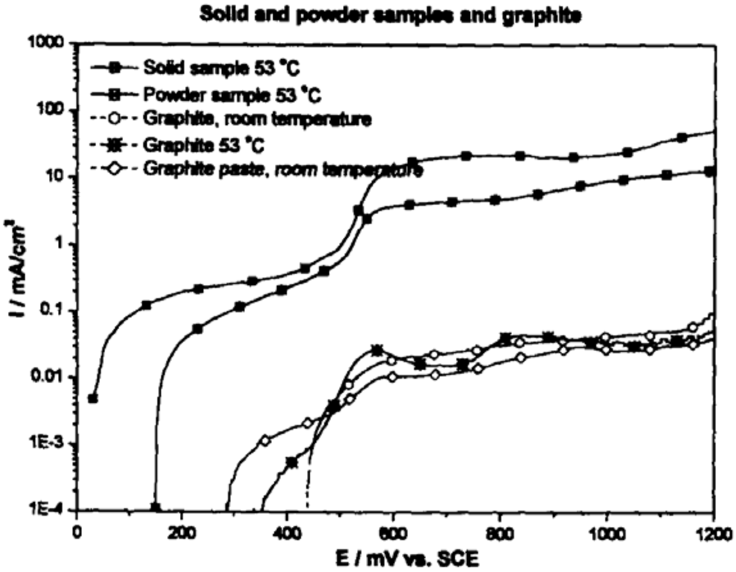

Fig. 5. Anodic polarization curves for solid Talvivaara sample, graphite paste electrode and graphites

At pH below 2 the sample showed clear areas of mineral transformations and sulphide dissolution. At these pH values mineral transformations happen at potentials below 500 mV vs. SCE. Mineral dissolution and release of sulphur, with or without oxidation to sulphate, happens at potentials above 500-550 mV. The beginning of mineral dissolution and sulphur release were observed for rapid current density increase. As the pH increases to 3 or more, the beginning of the mineral dissolution becomes less clear (Riekkola-Vanhanen et al. 2001). This is most likely related to reaction product layer formation (Pourbaix 1966).

Anodic polarization curves for solid and powder samples were measured in the temperature range 23-83 °C and at pH 1. The curve exhibited identical shapes (Figures 6 and 7). There is a clear change between temperatures 43 and 53 °C both for solid and powdered samples. Dissolution starts at lower potentials with increasing temperature and it becomes faster when temperature exceeds 53 °C.The current densities of powdered samples are lower than those of solid samples due to the smaller reactive area of the powdered sample surface. The solid sample has reactive surface of mineral only, whereas the powder sample surface includes also gangue.

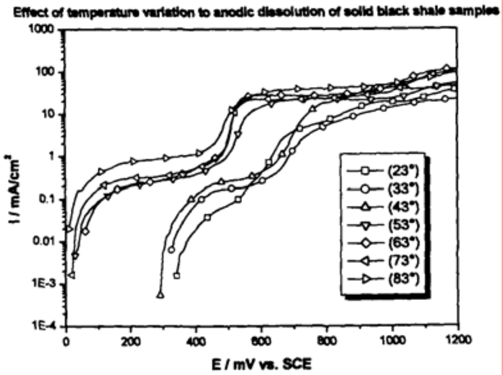

Fig. 6. Anodic polarization curves for solid Talvivaara samples at temperature range from 23 to 83 °C. Solution had $[CaSO_4 \cdot 2H_2O] = 2.41$ g/l, pH=1 and scan rate was 0.83 mV/s

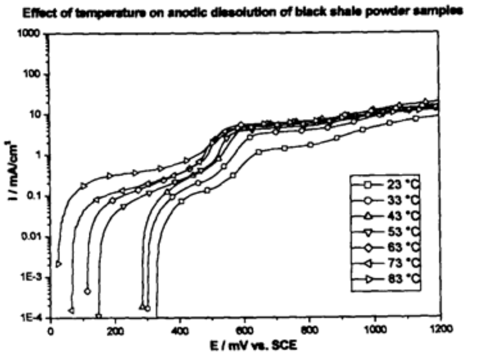

Fig. 7. Anodic polarization curves for powder Talvivaara samples at temperature range from 23 to 83 °C. Solution was in equilibrium with $[CaSO_4 \cdot 2H_2O] = 2.41$ g/l, pH=1 and scan rate was 0.83 mV/s

POTENTIOSTATIC MEASUREMENTS WITH TALVIVAARA ORE

The potentials at which the potentiostatic measurements were examined and selected from the anodic polarization curves. Upper potential limit was decided onducted by assumptions on the maximum redox potential that can be reached by common oxidants, such as oxygen or ferric iron. Potentiostatic experiments were in the potential range of 350-950 mV and at temperatures from 23 °C to 53 °C. Figures 8 and 9 show results of long potentiostatic measurements for solid and powdered Talvivaara samples, respectively. At all the chosen potentials it was observed that current density increased slightly with increasing temperature.

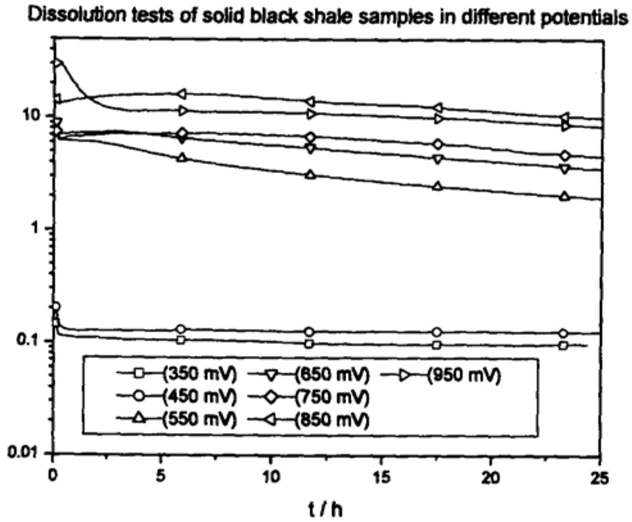

Fig. 8. Potentiostatic curves at T = 43 °C. Solution was saturated with $CaSO_4$ [$CaSO_4 \cdot 2H_2O$] = 2.41 g/l, pH = 1 and the potential range was from 350 to 950 mV

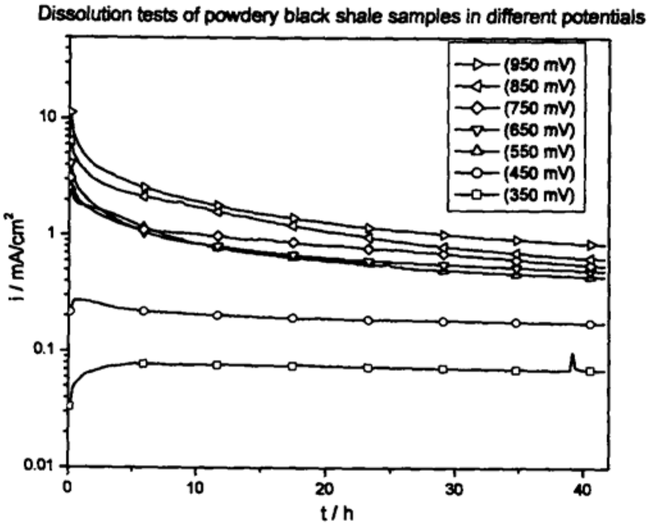

Figure 9. Potentiostatic curves at T = 43 °C. Solution was saturated with $CaSO_4$ [$CaSO_4 \cdot 2H_2O$] = 2.41 g/l, pH = 1 and the potential range was from 350 to 950 mV

The solutions of potentiostatic tests were analysed by the Geological Survey of Finland in Espoo by using inductively coupled plasma atomic emission spectroscopy (ICP-AES). For the solid samples the metal concentrations indicate that dissolution of iron sulphides increases significantly above 450 mV. Nickel and zinc dissolve slightly faster at potentials above 450 mV, but the effect is not very clear. The analyses were used to model the effect of potential and temperature. Linear regression analysis by using Microsoft EXCEL statistic data analysis package produced relationships shown in equations (1)-(5). The results are calculated separately for Cu, Ni, Fe, Zn and Mn. The functions are of the generic form $\ln[Me]$ (g/l) = $a \cdot 1/T$ (K) + $b \cdot E$ (mV) + c.

$$\ln[\mathrm{Cu}] = 110.9 \cdot 1/\mathrm{T} - 1.08 \cdot 10^{-3} \cdot \mathrm{E} - 3.912 \quad (1)$$

$$\ln[\mathrm{Ni}] = -1988 \cdot 1/\mathrm{T} + 3.45 \cdot 10^{-3} \cdot \mathrm{E} + 5.517 \quad (2)$$

$$\ln[\mathrm{Fe}] = -1914 \cdot 1/\mathrm{T} + 13.2 \cdot 10^{-3} \cdot \mathrm{E} + 2.783 \quad (3)$$

$$\ln[\mathrm{Mn}] = -1947 \cdot 1/\mathrm{T} + 0.78 \cdot 10^{-3} \cdot \mathrm{E} + 5.161 \quad (4)$$

$$\ln[\mathrm{Zn}] = -7657 \cdot 1/\mathrm{T} + 5.41 \cdot 10^{-3} \cdot \mathrm{E} + 20.41 \quad (5)$$

Statistical testing by F-test revealed that only the equations for iron, nickel and zinc had significance on the 95% confidence level. Further testing by t-test revealed that for these metals only the potential had significance and temperature had effect only for nickel.

The dissolution of powdered black shale samples were studied at potentials 350-950 mV at temperature 43 °C only. Comparison of dissolved metal concentrations (Table 2) indicates that copper dissolution increases by a factor of 3 to 20 at potentials 350-550 mV and by a factor of 50-80 at higher potentials. Dissolution of iron increases by a factor of ten at potentials 350-450 mV but it decreases by 50% at higher potentials. Dissolution of manganese increases by a factor of 10 to 70, but there is no clear potential dependence. The dissolution of nickel is about the same for powder and solid samples. Dissolution of zinc increases by a factor of 10 to 30 at potentials 350-450 mV but there is no clear change at higher potentials.

Table 2. Analyzed metal concentrations after potentiostatic experiments at $T = 43$ °C with powder samples, duplicate tests included. Tests have been done with 1 mm fraction

E (mV)	Cu, ppm	Fe, ppm	Mn, ppm	Ni, ppm	Zn, ppm	
350	0.225	55.9	26.7	3.06	3.06	
350	0.059	42.5	24.5	2.88	2.88	
450	0.245	52.6	26.1	3.04	3.04	
450	0.323	67.7	31.8	3.91	3.91	
450	0.491	76.6	24.5	3.41	3.41	
550	0.584	240	47.8	7.16	7.16	
550	0.613	170	4.4	3.76	3.76	3 mm fraction
650	0.523	191	38.7	6.46	6.46	
750	1.159	236	34.1	6.73	6.73	
850	4.939	332	33.5	8.79	8.79	
950	6.208	348	42.5	9.76	9.76	

Figure 10 shows the final current densities of potentiostatic curves for solid and powder samples. The curve shows the last 10 points at each potential plotted as current densities of powder sample vs. current densities of solid sample. The current densities of powder samples are lower, and the slope of the linear fit is 0.089.

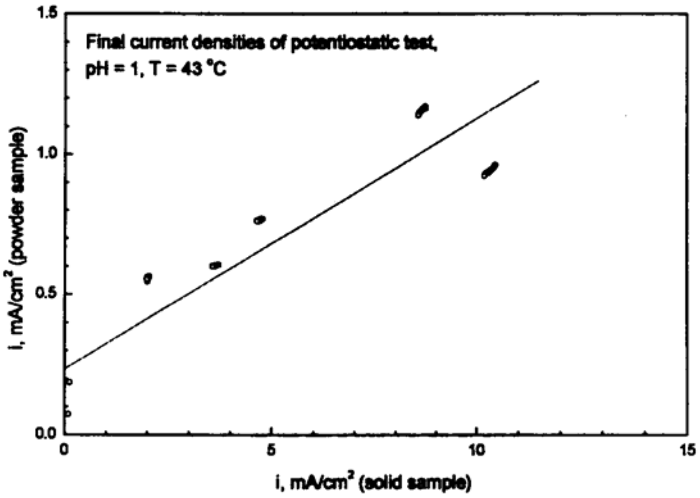

Figure 10. Final current densities correlation of solid and powder black shale samples at T = 43 °C. Solution was saturated with $CuSO_4$ $[CaSO_4·2H_2O]$ = 2.41 g/l, pH = 1 and the potential range from 350 to 950 mV

TESTS WITH LUBIN BLACK SHALE ORE AND CONCENTRATE

The powdered samples of Lubin black shale materials were studied using the developed carbon paste electrode. The composition of the material is given in Table 3. The ore contains high Cu contents in thin deposit what results from high percentage of strongly mineralised shale ore. The composition of the Lubin concentrate was not given.

Table 3. The chemical composition of copper ore (shale) in Polish copper deposit (KGHM „Polish Copper”, unpublished data)

Fe, ppm	Ni, ppm	Cu, ppm	Zn, ppm	Mn, ppm	Co, ppm
9330	278	104800	780	947	189

Because the metal sulphides are finely disseminated in the carbonate matter (about 18% $CaCO_3$) a sulphuric acid treatment was used to enhance dissolution. Acidic non-oxidative leaching of the shale ore or concentrate involves chemical reactions between sulphuric acid and calcium or magnesium carbonates. The reactions (6) and (7) dominate during the non-oxidative leaching:

$$CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4{\cdot}2H_2O\downarrow + CO_2\uparrow \quad (6)$$

$$MgCO_3 + H_2SO_4 \rightarrow MgSO_4 + H_2O + CO_2\uparrow \quad (7)$$

The leaching of a carbonate gangue with H_2SO_4 is a very fast chemical process and can be performed at ambient temperatures. The consumption of sulphuric acid was followed by looking for the production of carbon dioxide bubbles. Carbon dioxide, evolving in reactions (6) and (7), creates an oxygen-free atmosphere preventing the undesirable disolution of valuable metals (Cu, Zn, Ni, Co, Mn) from the sulphidic raw material. After the acid treatment desired amount of shale or shale concentrate was crushed and used to prepare GPE for electrochemical examination

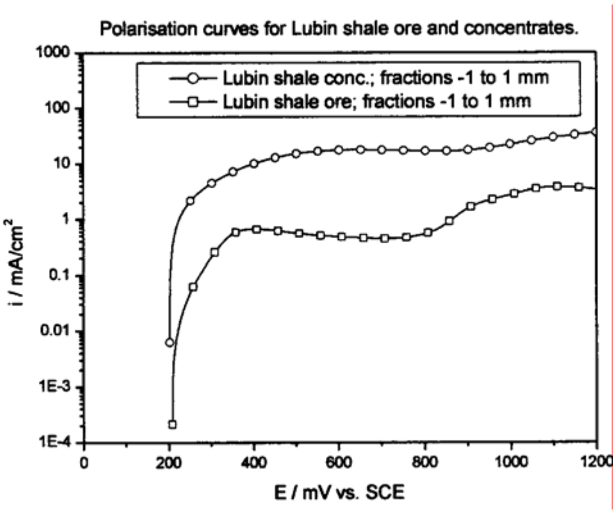

Fig. 11. Anodic polarization curves made at pH 1. Solution composition was $[CaSO_4{\cdot}2H_2O] = 2.41$ g/l, T = 23 °C and scan rate was 0.83 mV/s

The dissolution of powdered Lubin shale and shale concentrates samples were studied with polarization curves and potentisotatic tests in the potential range of 500-900 mV and at temperature 23 °C. Polarisation curves are shown in Figure 11. The dissolution begins almost immediately when the sample potential is increased. The current density does not change much. The same dissolution stages and mechanisms as with Talvivaara ore are not seen. The current densities for Lubin ore are of the same magnitude as for Talvivaara ore, but the current densities of Lubin concentrate are ten times higher. Potentistatic curves for Lubin ore and concentrate at selected potentials are shown in Figure 12. The current densities for Lubin ore are lower as for Talvivaara ore, but the current densities of Lubin concentrate are slightly times higher. The curves reach fairly soon a steady state indicating formation of a reaction product layer and the controlling mechanism is mass transfer through the layer.

Analyzed metal concentrations after potentiostatic experiments were done by the Geological Survey of Finland in Espoo by using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The analysis results for Lubin ore and concentrate are shown in Table 4. The experiments shown in Table 4 are the same as in Figure 12.

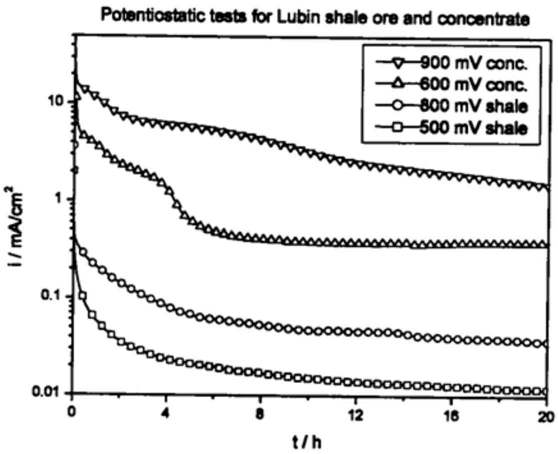

Fig. 12. Potentiostatic curves at $E = 500$, 600, 800 and 900 mV vs. SCE. Solution was saturated with $CuSO_4$ $[CaSO_4 \cdot 2H_2O] = 2.41$ g/l, pH = 1 and the temperature was 23 °

Table 4. Chemical analysis of Lubin ore and concentrate after potentiostatic dissolution tests.

E (mV)	Sample	Cu, ppm	Fe, ppm	Mn, ppm	Ni, ppm	Zn, ppm	Co, ppm
500	shale	34.7	5.9	0.2	15.3	0.53	0.13
800	shale	178	21.7	0.32	1.08	1.13	1.67
600	conc.	293	142	1.47	2.05	3.43	4.97
900	conc.	487	373	2.93	7.65	6.9	9.47

The results in Table 4 indicate that leaching of the concentrate is more efficient than leaching the ore. Improved dissolution rates will be gained by using potentials of 600 mV or more. A possible way to limit iron dissolution is to use ore instead of concentrate and limit the leaching potential.

CONCLUSIONS

The dissolution characteristics of Talvivaara and Lubin black shale minerals were studied with special anode construction, where the powdered samples where mixed with fine particles of graphite and binding components. The sample preparation from powdered mineral has to be done by special procedure in order to obtain reproducible results with respect to solid samples. The electrochemical experiments with Talvivaara ore showed good reproducibility despite the active surface can vary significantly due to its porous character. During electrochemical testing it was noticed that even though the calculated current densities are higher for solid electrodes, the actual dissolved metal contents are higher for powder samples. The metal recoveries from powdered samples were ten times higher than from solid samples. With powder samples the selectivity of valuable metals (other than Fe) was better than with solid samples.

The dissolution of the Lubin black shale and shale concentrate were examined by using the same GPE method as for Talvivaara ore. After an acid treatment a desired amount of shale or shale concentrate sample was used to make a GPE. To verify the applicability of a newly prepared GPE, potentiodynamic and potentiostatic measurements were carried out. The described method of preparing a graphite paste electrode provides a useful tool for the study of electrochemical dissolution behaviour of sulphide minerals, regardless of their origin.

ACKNOWLEDGEMENT

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REFERENCES

ADAMS, R.N., 1958, *Carbon paste electrodes.* Analytical Chemistry(Scientific Communications), 1(30): p. 1576.

AHLBERG, E.A., J., 1993, *Carbon paste electrodes in mineral processing: an electrochemical study of galena.* Hydrometallurgy, 1993(34): p. 171-185.

FORSÉN, O., ANTILA, E., AROMAA, J., PESONEN, P., 1996, *Evaluation of carbon paste electroactive electrode for the electrochemical characterization of sulphide minerals.* Acta Metallurgica Slovaca 2, 1996(1): p. pp. 7-18.

GERLACH, J., KÜZECI, E., 1993, *Aplication of carbon paste electrodes to elucidate hydrometallurgical dissolution processes with special regard to chalcocite and covelite.* Hydrometallurgy, 1983(11): p. 345-361.

KINOSHITA, K., 2001, *Electrochemical uses of carbon*.

KUHN, A.T., 1987, *Techniques in Electrochemistry.* Corrosion and Metal Finishing, p. 66 p.

LOUKOLA-RUSKEENIEMI, K., et al., 1999, *Environmental impact of metalliferous black shales at Talvivaara in Finland, with indication of lake acidification 9000 years ago.* Journal of Geochemical Exploration, 64(1-3): p. 395-407.

POURBAIX, M., 1966, *Atlas of Electrochemical Equilibria in Aqueous solutions*, ed. P. Press., Bristol. 386.

RICE, M.E., GALUS, Z. and ADAMS, R. N., 1983, *Graphite paste electrodes. Effect of paste composition and surface states on electron-transfer rates.* Journal of Electroanalytical Chemistry, 1983(143): p. 89-102.

RIEKKOLA-VANHANEN, M., et al., 2001, *Effect of pH on the biological leaching of a black schist ore containing multiple sulfide minerals*. in *Biohydrometallurgy: Fundamentals, Technology and Sustainable Development*..

SVANCARA, I., SCHACHL, K., 1999, *Testing of unmodified carbon paste electrodes.* Chemiche Listy, 1999(93): p. 490-499.

Galfi I., Aromaa J., Forsen O., *Laboratoryjne narzędzie do elektrochemicznych badań minerałów siarczkowych,* Physicochemical Problems of Mineral Processing, 41 (2007) 301-312 (jęz. ang.).

Roztwarzanie minerału siarczkowego w roztworach wodnych zachodzi na drodze różnych mechanizmów. Szybkość całkowitej reakcji jest kontrolowana przez szybkość najwolniejszego etapu reakcji. Najważniejszym czynnikiem w anodowym rozkładzie minerałów siarczkowych jest tworzenie warstwy produktu reakcji, która wpływa na szybkość wymiany masy na granicy faza stała – roztwór, która jest często etapem kontrolującym proces roztwarzania minerału. W tej pracy użyliśmy elektrochemicznej metody oceny podatności surowców siarczkowych na proces ługowania. Jako podstawowe narzędzie tej metody zastosowaliśmy pomiary elektrochemiczne na elektrodach wykonanych z badanego surowca. Elektrody użyte w pomiarach są wykonane w postaci pasty z udziałem grafitu i drobnoziarnistego materiału siarczkowego. Taka konstrukcja elektrody zapewnia warunki bliskie tym, jakie występują w rzeczywistym procesie ługowania. Grafitowa elektroda w formie pasty zawierającej siarczki metali gwarantuje dużą powtarzalność i niezawodność.