

Exposure tests of copper foils in a slurries of different bentonites

Expoziční testy měděných folií v suspenzích různých bentonitů

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The goal of the study was to compare corrosion performance of copper in different bentonite slurries. Copper coil samples were exposed in a slurries of bentonites BaM, Rokle, B75, G2M, Voltex, Sabil. The test was carried out under anaerobic conditions in glovebox at laboratory temperature for duration of one to four months. Samples were evaluated by means of X-ray diffraction and mass loss. Liquid parts of slurries were analysed by ion chromatography and pH meter. The resistance of copper in all studied bentonites was very high. Corrosion rates were in order of tenths of micrometers per year. No trend between pore solution composition and corrosion rate or composition of corrosion products was observed.

Cílem této práce bylo porovnání korozní odolnosti měděných folií v suspenzích různých bentonitů. Cívkové měděné vzorky byly exponovány v suspenzích bentonitů BaM, Rokle, B75, G2M, Voltex, Sabil. Expozice probíhala za anaerobních podmínek v rukavicovém boxu za laboratorní teploty po dobu jednoho a čtyř měsíců. Vzorky byly hodnoceny pomocí rentgenové difrakce a hmotnostních úbytků. Kapalná část suspenzí byla analyzována pomocí iontové chromatografie a měření pH. Agresivita všech studovaných bentonitů k mědi byla zanedbatelná. Korozní rychlosti byly v řádu desetin mikrometrů za rok. Nebyl pozorován žádný vliv složení pórového roztoku na korozní rychlost nebo složení korozních produktů.

INTRODUCTION

Copper is material believed as corrosion resistant in wet bentonite environment of radioactive waste deep geological repositories. It is candidate material for outer case in Scandinavian concept [1-5] and for coating in Canadian [6-10]. Copper is also one of the candidate materials for construction of canisters in Czech concept [11-18]. In previous works we studied the effect of sulphide content on corrosion rate of copper in bentonite pore solution [18] and simulation of galvanic couple with carbon steel [14].

The aim of this study was to compare behaviour of copper in different bentonites in short-term experiments.

EXPERIMENTAL

Copper foil of the thickness 100 μm and purity 99.97 wt.% (GoodFellow) was used for samples preparation. Each sample had dimensions 50 \times 300 mm. Six types of bentonite were used as environments: BaM, Rokle, B75, G2M, Voltex and Sabil. 200 g of each bentonite was mixed with 1000 ml of demineralised water in 1000 ml glass flask and deaerated for 2 weeks in glovebox by nitrogen (99.99 vol.%). Part of slurry was deposited on the foils as 1 mm thick layer and then

close packed in a coils. Two coils were exposed in each flask. Foils were weighed on analytical scales before and after the exposure. Experiments were carried out at laboratory temperature (T_{LAB}). One sample from each flask was removed after 1 month exposure; the second after 4 months. Some samples were studied by means of X-ray diffraction (XRD). Finally, all samples were pickled in solution of sulfuric acid (5 wt.%) for 5 minutes and weighed. Liquid parts of slurries were filtered and analysed by means of ion chromatography and pH meter.

RESULTS AND DISCUSSION

The swelling of bentonites resulted in different liquid portion of the slurry which was extracted for analyses (see Tab. 1). Bentonites BaM, Rokle and Sabil provided significant volume of liquid part, B75 and Voltex significantly lower volume and G2M absorbed all water forming the gel part of the slurry. Therefore, pH and ion chromatography could not be performed in the G2M slurry. Values of pH were approximate measures of bicarbonates/carbonates content. Among other bentonites, the only exception was bentonite B75, which was activated during manufacture by addition of sodium carbonate. Major anion component of the

slurry pore solution was sulphate. Almost all bentonites contained about 10^{-4} mol.dm⁻³, amount of sulphates in Voltex was one order higher. Sabenil and Voltex had slightly higher content of chlorides, compared to the others. The significant differences were in nitrates. Concentrations in BaM, Voltex and B75 were measurable, but undetectable in Rokle and Sabenil.

The appearance of the samples and local XRD data are summarised in Fig. 1. All samples were attacked uniformly. Despite some localized precipitation of different corrosion products, especially on samples BaM, Rokle and Voltex, no penetration into the material was observed after the pickling procedure. The presence of

tenorite and malachite under anaerobic conditions is of interest. Cuprous corrosion products are usually detected under such conditions. It was obviously independent on a content of nitrates, since Sabenil bentonite which was free of nitrates showed the highest content of tenorite after the exposure. This could be action of ferric cations leached from the bentonites, but their analysis in the slurry is extremely difficult. Content of malachite was also not related to the content of carbonates since the content of malachite on the surface of B75 sample was limited. Precipitation of corrosion products was probably influenced by the local composition of pore solution, which could not be analysed in the bulk.

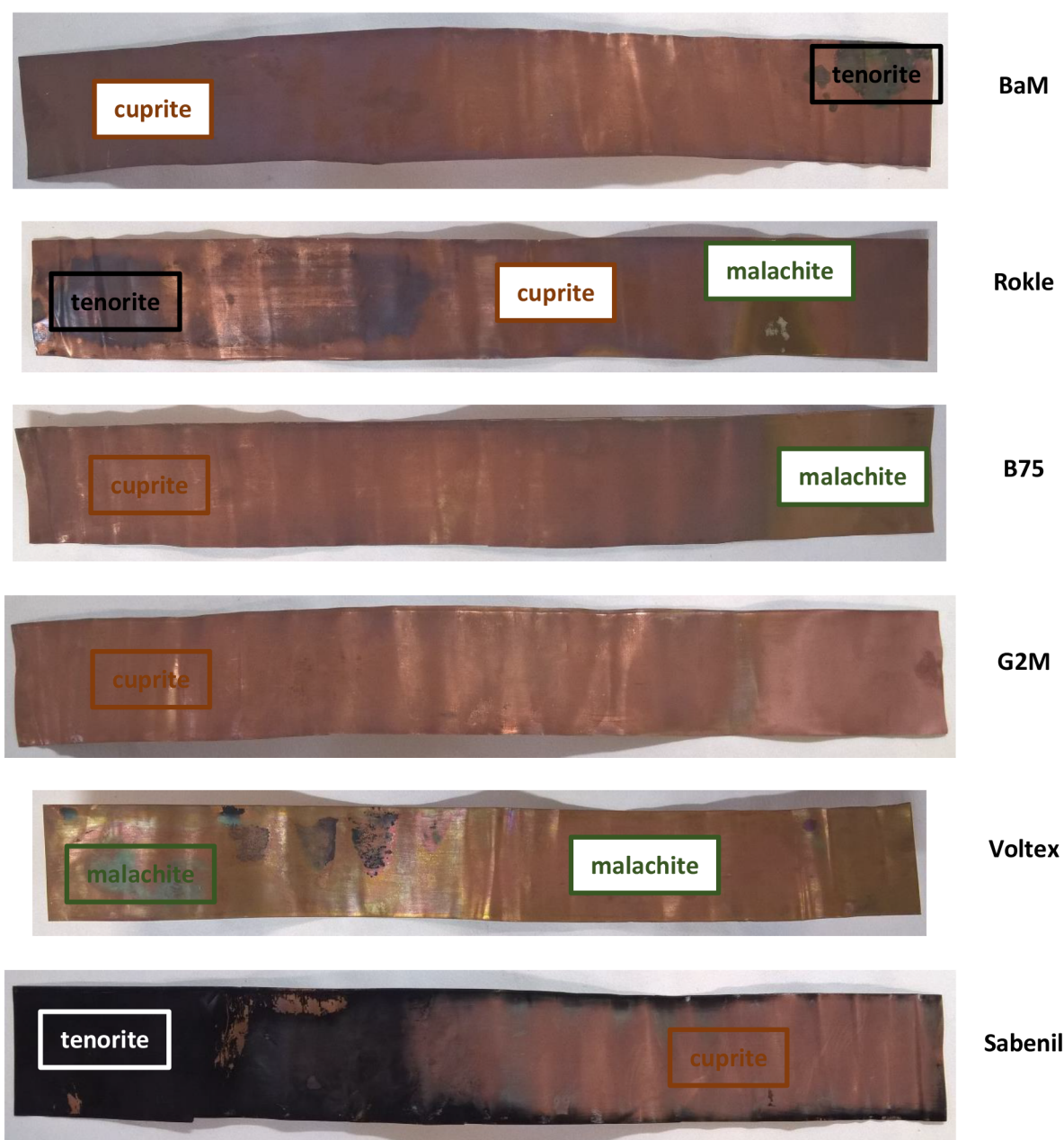


Fig. 1. Appearance of the samples after 4 month exposure and local XRD analyses

Obr. 1. Vzhled vzorků po 4 měsíční expozici a lokální rentgenově difrakční analýzy

Tab. 1. Composition of slurry liquid part after the 4 month exposure / Složení kapalné části suspenzí po 4 měsíční expozici

Bentonite	Vol. of liquid	pH	fluoride	chloride	nitrate	sulphate
	[ml]		[mol dm ⁻³]			
BaM	580	8.5	2.72 10 ⁻⁵	7.01 10 ⁻⁵	2.90 10 ⁻⁵	1.85 10 ⁻⁴
Rokle	550	8.6	5.67 10 ⁻⁵	6.06 10 ⁻⁵	< 4.84 10 ⁻⁷	3.63 10 ⁻⁴
B75	100	9.3	4.67 10 ⁻⁵	8.68 10 ⁻⁵	5.79 10 ⁻⁵	1.60 10 ⁻⁴
G2M	–	8.3	–	–	–	–
Voltex	200	8.6	6.94 10 ⁻⁵	1.57 10 ⁻⁴	8.31 10 ⁻⁵	4.00 10 ⁻³
Sabenil	485	8.4	3.44 10 ⁻⁵	1.93 10 ⁻⁴	< 4.84 10 ⁻⁷	1.30 10 ⁻⁴

Tab. 2. Summary of the mass loss evaluation / Souhrn vyhodnocení hmotnostních úbytků

Bentonite	Corrosion rate [μm a ⁻¹]	
	1 month	4 months
BaM	0.35	0.27
Rokle	0.35	0.43
B75	0.12	0.26
G2M	0.31	0.32
Voltex	0.39	0.32
Sabenil	1.01	0.53

Estimated mass loss corrosion rates are summarised in Tab. 2. All samples showed corrosion rate in order of tenths of μm.a⁻¹ after the 4 months of exposure. Influence of pore solution composition on dissolution rate within the short term exposure is rather negligible. It could become important in long-term exposures, when more voluminous corrosion products could seal the bentonite pore system efficiently, decreasing the transport ability and consequently the corrosion rate.

CONCLUSIONS

No significant effect of bentonite pore solution composition on corrosion rate was observed within 4 months exposure. In addition, no significant effect of the bulk bentonite pore solution on the composition of corrosion products was observed. There were most likely local compositions which played more important role in precipitation of corrosion products.

Acknowledgement

This work was supported by SÚRAO (Czech Radioactive Waste Repository Authority) under Project No. SO2013-088.

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