Desalting of Acid Mine Drainage by Reverse Osmosis Method – Field Tests

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ABSTRACT

Acid mine drainage (AMD) from brown coal opencast mines in the Czech Rep. is mainly characterized by increased concentrations of sulphates, calcium, iron, manganese, non-dissolved substances and in some cases low values of pH. AMD is treated before discharging within the following range: neutralization – de-ironing – removal of non-dissolved substances. Decreasing the sulphates and calcium concentration is currently not performed.

During the last year the short-time desalting field test of AMD by the reverse osmosis method was performed with three different sources of AMD. It was discovered that the technology of reverse osmosis could be used for recovering good quality water (e.g. for industry) from AMD.

Basic information about AMD in the Czech Rep., using routine methods for their treatment, technical specifications and the results of desalting field test acid mine drainage by the reverse osmosis method are presented.

BASIC INFORMATION ABOUT MINE WATERS FROM BROWN COAL OPENCAST MINING

Brown coal (or soft-coal, not lignite) is an important raw material for the Czech Republic and is almost purely used for energy production. *In Figure 1* there is a diagram of a proportion of energy resources in electric energy production in the Czech Republic in the year 2003 and in *Figure 2* a diagram of a proportion of fossil fuels used for the electric power production in this year (Czech Statistical Office, 2005).



Figure 1: Proportion of sources in the Czech Republic electric power production from the year 2003. *)

Brown coal is currently mined only at the opencast mines in the Czech Republic. That is at 7 mines in two areas situated in the western part (Sokolov Brown Coal Basin) and the north-western part (North-Bohemia Brown Coal Basin) of the Czech Republic. In the Czech Republic there are other deposits of brown coal and lignite which are, regarding their size, not significant. In the Czech Republic average exploitation of brown coal and lignite ranged from 49 to 51 tonnes a year in the period of 2000 - 2003.

Opencast mine operation and the existence of underground mines, where mining is not in progress, are related to the occurrence of great amount of variously polluted mine waters. There are estimated that each year ca 10 - 12 million m³ mining waters are drained to the drainage canals in two biggest brown coal districts of the Czech Republic.

Mine water pollution is very changing and generally saying opencast mine waters are more polluted than underground mine ones. One of the reasons for this condition may be the fact that underground mines used to be opened mainly in the locations with good quality coal and low content of sulphur. The second reason is, mainly from the content of undissolved solids in mine waters perspective, another manner of mine water occurrence and collection from opencast and underground mines.



Figure 2: Proportion of various types of fuels in electric energy production at the Czech Republic heat power plants from the year 2003 *)

As well as in other areas also here the presence of brass and/or white iron pyrite in coal and in overburden materials is the cause of "chemical" pollution of mine waters. In *Table 1* typical pollution of mine water pumped from the detention reservoirs at the bottom of the opencast mines to the mining water treatment plants or recipients is introduced. Extreme values found in some mine waters and limit concentrations defined by the Act (No. 254/2001 Coll.) to regulate mine water discharge has been also introduced.

With respect to local conditions a water using authority can define some other relevant quality parameters for mine water discharge in the locations, mainly dissolved solids and NH_4^+ , but also other indicators (total petroleum hydrocarbons, metals et al.).

			Typical pollution	Extreme concentrations	Limit concentrations
	рН		5 – 9	2,5	6 - 9
	Fe _{tot.}	mg/L	<0,1 - 30	700	3
	Mn	mg/L	<0,1 - 5	50	1
•	SO4 ²⁻	mg/L	400 – 2 500	4 000	Not defined
	PAH.	mg/L	<0,001		0,01
	Und. sol.	mg/L	<5 - 200	20 000	40
	Dis. sol.	mg/L	600 – 3 500	6 000	Not defined

(PAH - polyaromatic hydrocarbons; Und. sol. - undissolved solids; Dis. sol. - dissolved solids)

Table

Typical Pollution of Mine Waters from Opencast Brown Coal Mines, Extreme and Limit Concentrations Defined by Law.

Most mine waters from opencast mines are currently treated before being discharged. In case of need the following processes are used for mine water treatment:

- pH adjustment (dosage mainly CaO)
- Iron and manganese removal (pH adjustment aeration deposition)

> Undissolved solids removal (natural deposition, using flocculants in some cases)

Dissolved solid content decreasing is an unresolved issue in the treatment of mine waters from brown coal opencast mines. Though the Law in the Czech Republic does not define a limit concentration for sulphates or dissolved solids in discharged mine waters but this option as stated beforehand exists. In one case the water using authority has already indicated that under certain conditions they will request dissolved solid content decrease in discharged mine waters.

The processes to decrease sulphates or dissolved solid concentrations are generally known and some of them have been verified under laboratory conditions in the Czech Republic (sulphate precipitation with Al^{3+} and Ca^{2+} ions, sulphate precipitation with Ba^{2+} ions, biological removal of sulphates, some diaphragm processes). None of the technologies has been performed under the operation conditions of opencast mines mainly for two reasons:

1) Quite high investment and/or operation costs;

2) This mine water treatment process has not been strictly requested by the water authority.

1:

Mine waters are not the only negative impacts of mining on environment but can also be a significant source of quality water for industry, agriculture, recreation etc. A large scale programme for refurbishment and restoration of landscape affected with opencast coal mining starts to be implemented in the Czech Republic supported by the government of the Czech Republic, too. In the framework of this programme using "new" landscape for recreation, industrial plant growing etc. is expected, but a construction of new industrial zones with labour opportunities has been planned and implemented in these areas as they are affected with mining and are characterized with high unemployment (consequences after total transformation of Czech industry after the change of political system in 1989). All these are projects which will require sufficient amount of quality water.

But in the Czech Republic in the areas affected with opencast coal mining significant natural sources of quality surface water do not exist and e.g. water for heat power plants, a significant petrochemical plant and other industrial plants located in the North-Bohemia Brown Coal Basin must be transported via pipeline from the sources several tens of kilometres distant.

Therefore it is obvious that mine waters can be approached in two ways:

- 1) Mine waters must be treated before being discharged to meet the defined limit concentrations for their discharge and not to consequently worsen the quality of surface waters;
- 2) Mine waters can be generally treated and then used as the water sources for new industry, reclamation of the area affected with opencast mining etc.

Pilot tests for desalting mine waters with reverse osmosis were proposed and performed for primary verification if this up-to-date and progressive method of water treatment can be considered for specific polluted mine water treatment (variable content of undissolved solids – coal dust, sands, clays; Ca – SO₄²⁻ balanced system; various forms of iron occurred – Fe²⁺, Fe³⁺, Fe(OH)₃(\downarrow) etc.).

PILOT TESTS IMPLEMENTATION AND RESULTS

Three various locations were selected to implement pilot tests:

Location **A**: Mine water from a retention basin was used for the pilot test from which the water is pumped to a process equipment of mine water treatment plant; mine water treatment is, in this location, solved so that all mine waters from the places of their occurrence are conducted without treatment to a retention basin. As a consequence of a certain detention period partial pre-preparation of mine waters takes place (depositing of undissolved solids; change in forms of iron occurrence: $Fe^{2+} \rightarrow Fe^{3+} \rightarrow Fe(\downarrow)$);

Location **B**: Untreated mine water with higher content of iron and manganese was used for the pilot test; mine water is, without treatment, discharged to surface waters;

Location C: Mine water drained from the mine water treatment plant was used for the pilot test; mine waters from the retention basin at the bottom of the mine are pumped to this mine water treatment plant where in case of need pH is adjusted, fine bubble aeration is performed ($Fe^{2+} \rightarrow Fe^{3+}$) and a flocculant is dosed to increase the efficiency of undissolved solids removal.

		Location A	Location B	Location C
PH		7,2	6,8	8,7
Fe _{tot.}	mg/L	1,1	10,5	1,5
Mn	mg/L	4,4	2,2	1,6
SO4 ²⁻	mg/L	1900	1020	903
Dis. sol.	mg/L	2920	1700	1610
Са	mg/L	330	290	220
Mg	mg/L	134	112	120
NH4 ⁺	mg/L	8,2	11,5	6,6
Zn	mg/L	0,05	< 0,04	< 0,04
Ni	mg/L	< 0,1	< 0,1	< 0,1
V	mg/L	0,04	0,02	0,009
As	mg/L	< 0,003	< 0,003	< 0,003
Со	mg/L	< 0,09	< 0,09	< 0,09
Cu	mg/L	< 0,04	< 0,04	< 0,04
Ва	mg/L	0,07	0,05	0,04

Chemical composition of mine waters used for pilot tests is stated in Table 2.

Table 2: Chemical Composition of Mine Waters Used for Pilot Tests.

Pilot tests were performed at the reverse osmosis equipment located in a mobile container. The tests ran at the locations under the following conditions:

- during all tests only one type of diaphragms were used for the reverse osmosis technology`
- > the output of the pilot equipment was $0.8 \text{ m}^3/\text{h}$
- > the whole system was able to operate up to the pressure 65 bar.

		crude mine water	permeate (04.08.25; 14:00)	concentrate (04.08.25; 14:00)
PH		7,2	4,2	7,0
Fe _{tot.}	mg/L	1,1	< 0,1	0,2
Mn	mg/L	4,4	< 0,05	5,4
SO4 ²⁻	mg/L	1900	1	2290
Dis. sol.	mg/L	2920	66	3510
Са	mg/L	330	0,2	420
Mg	mg/L	134	0,06	159
NH_4^+	mg/L	8,2	0,2	10,5
Zn	mg/L	0,05	< 0,04	0,06
Ni	mg/L	< 0,1	< 0,1	< 0,1
V	mg/L	0,04	< 0,006	0,03
As	mg/L	< 0,003	< 0,003	< 0,003
Со	mg/L	< 0,09	< 0,09	< 0,09
Cu	mg/L	< 0,04	< 0,04	< 0,04
Ва	mg/L	0,07	< 0,006	0,08

The results acquired from pilot tests concerning chemical composition of permeates and concentrates are stated in *Table 3* to 5.

Table 3: Location A – Results of Pilot Tests

		crude mine water	permeate (04.08.30; 15:30)	concentrate (04.08.30; 15:30)
pН		6,8	4,3	6,3
Fe _{tot.}	mg/L	10,5	< 0,1	21,6
Mn	mg/L	2,2	< 0,05	5,7
SO4 ²⁻	mg/L	1020	7	2960
Dissolv. subst.	mg/L	1700	116	4830
Са	mg/L	290	0,4	700
Mg	mg/L	112	0,09	260
NH_4^+	mg/L	11,5	0,9	28
Zn	mg/L	< 0,04	< 0,04	0,34
Ni	mg/L	< 0,1	< 0,1	< 0,1
V	mg/L	0,02	< 0,006	0,06
As	mg/L	< 0,003	< 0,003	< 0,003
Со	mg/L	< 0,09	< 0,09	< 0,09
Cu	mg/L	< 0,04	< 0,04	< 0,04
Ва	mg/L	0,05	< 0,006	0,10

Table 4: Location B – Results of Pilot Tests

		crude mine water	permeate (04.09.02; 12:00)	concentrate (04.09.02; 12:00)
pН		8,7	4,8	7,5
Fe _{tot.}	mg/L	1,5	< 0,1	< 0,1
Mn	mg/L	1,6	< 0,05	3,3
SO4 ²⁻	mg/L	903	18	3900
Dissol. subst.	mg/L	1610	180	6320
Са	mg/L	220	0,6	700
Mg	mg/L	120	0,07	350
NH_4^+	mg/L	6,6	0,4	22
Zn	mg/L	< 0,04	< 0,04	0,06
Ni	mg/L	< 0,1	< 0,1	< 0,1
V	Mg/L	0,009	< 0,006	0,05
As	mg/L	< 0,003	< 0,003	< 0,003
Со	mg/L	< 0,09	< 0,09	< 0,09
Cu	mg/L	< 0,04	< 0,04	< 0,04
Ва	mg/L	0,04	< 0,006	0,13

Table 5: Location C – Results of Pilot Tests

Note: - all stated results relate to single samples taken;

- during the field tests mass balance of the components was not performed.

During the pilot testing the impact of reverse osmosis process to microbiological indicators was also monitored. *Table 6* states the results of microbiological analysis of crude mine water and permeate from the location A.

		crude mine water (04.08.24; 10:50)	permeate (04.08.24; 10:50)
Escherichia Coli	KTJ/100 ml	200	0
Coliform bacteria	KTJ/100 ml	400	7
Number of coloni (22 ⁰ C)	es KTJ/ml	1 680	94
Number of coloni (36 ⁰ C)	es KTJ/ml	1 520	48
Abioseston	%	30	1
Live organisms	individuals/ml	126	0
No. of organisms	individuals/ml	136	0

Table 6: Location A – Results of Crude Mine Water and Permeate Microbiological Analysis

In water treatment regardless the type of technology used, it is necessary to solve the issue of generated waste processing and disposal. That, of course, applies for diaphragm processes when it is necessary to solve the issue of a concentrate generated. When desalting sea water to potable water the solution is simple as the concentrate returns to the sea. In case of desalting mine waters it will be more complicated. If the main intension of the reverse osmosis process use in desalting mine waters is to acquire quality water for industrial use, then under certain conditions the concentrate may be discharged to surface waters. From environment protection perspective could be assume that water using authorities would require another solution for processing the concentrate without direct impact on environment.

The pilot testing of mine waters desalting performance is followed with the second part of the project focusing on the concentrate processing. In the course of pilot tests 100 I of concentrate was sampled for the follow up laboratory tests. To process the concentrate its mixing with ash which is caught from the desulphurizing flue gases of the heat power plants and which contains to 30% free CaO has been proposed. Based on the current experience with chemical features of some flue gases a mixture similar to concrete may arise after mixing suitable amount of the concentrate and ash. The cations and anions from the concentrate are closely fixed in that mixture and will not eluate with precipitation into surrounding environment when depositing e.g. to deposits or suitable areas in opencast mines. The results of the solution in this part of the project will be available by the end of the year.

SUMMARY OF RESULTS FOR PILOT TESTS

> Pilot testing in all three locations proved that treating mine waters from opencast brown coal mining with reverse osmosis process is currently possible from technical perspective;

> In spite of the testing targets not being to reach minimum and/or maximum possible concentration of substances in permeate and/or concentrate, the test results may be considered favourable because the concentration of the monitored substances in the permeates were very low (mainly dissolved substances, sulphates, calcium, magnesium, manganese and ammonium);

> All tests were run under the stable operation conditions and in the course of the tests no operation issues occurred;

> The pilot testing proved that reverse osmosis process improves microbiological properties of mine water; the microbiological analysis proves that the permeate (dated 4.8.2004) meets the requirements for potable water determined by the law in the Czech Republic;

➤ To acquire necessary amount of data for the proposal of the actual reverse osmosis process into operation conditions of opencast brown coal mines a pilot test with the duration of ca 1 month has been proposed. The pilots tests were performed in the framework of the project "Research after the possibility of desalting acid mine drainage by the method of reverse osmosis", the solution of which in the years 2004 – 2005 has been financially supported by the Grant Agency of the Czech Republic (project No: 105/04/1533).