



Mine water treatment with yellowcake by-production

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Abstract. Mining and milling of uranium ore in Hungary was terminated at the end of 1997. From that time rehabilitation works have been carrying out, which include mainly the relocation of different solid wastes, such as waste rocks, heap leached residues, demolishing of former industrial buildings, clean up contaminated sites. Overall rehabilitation of the tailings ponds has also started. At first step the ground water restoration system is under construction, aiming at protecting the drinking water aquifer situated in the immediate vicinity of the tailings ponds. Former mining activity has been carried out also in the vicinity of the drinking water catchment area, for protection of that is compulsory to maintain appropriate depression in the mine in question. This means that mine water has to be pumped out continuously and because of the elevated uranium concentration in mine water, the water has to be treated. Thus the water quality protection is connected with uranium removal from the mine water. Mine water treatment process developed is based on anion-exchange process and removal of the uranium from the eluates with hydrogen peroxide.

1. HISTORICAL OVERVIEW ON THE MINING AND PROCESSING ACTIVITY

Exploration of uranium ore started in Hungary in 1953. Soon after first air gamma measurements it became clear that near the town Pécs significance uranium deposit is situated. After intensive exploration works in 1954 a company was established and at the end of the fifties mining activity started.

During operation period about 46.8 million tons of rock has been removed from 5 shafts situated on the same mining district.

From the mined out rock 18 million tonnes as waste rock ($U < 100$ g/t) was placed on 10 waste rock piles (some of them were small). 7.2 million tons of low-grade ore ($U = 100-300$ g/t) after crushing to - 30 mm was treated by alkaline heap leaching on isolated area. Almost 19 million tons of ore ($U = 1000$ g/t) was processed in the conventional mill built in 1962, using sulphuric acid for leaching.

During the mining activity approximately 64-million m^3 mine water was pumped out from the mines, from which about 30 million m^3 mine water were used in the mill.

The neutralised waste pulp from the mill was pumped to the tailings ponds (two tailings ponds were built). Total uranium production from the district was a little more than 20 thousand tons.

2. HYDROLOGIC CONNECTION OF THE MINES WITH DRINKING WATER CATCHMENT AREA

The company had 5 shafts, from which shaft No. 1 has a direct connection with the drinking water aquifer. Therefore even after closing the shaft No. 1 in 1968 for protection of the drinking water aquifer it was prescribed by the authorities to continue water pumping from the mine, for keeping water level in the former mine at 107 m below the surface, assuring appropriate depression around the mining area. This prescription is still in force. This is the reason why the water is still pumped out from the mine even after 32 years of its closing.

3. MINE WATER TREATMENT PROCESS

Composition of mine water is presented in Table 1. It can be seen that the pH of water is neutral, sulphate; bicarbonate, calcium and sodium are the dominant components. Arsenic and other heavy metals are present only in a very small concentration. Radium content is about 0.4 Bq/l, much below the discharge limit (1.1 Bq/l).

Historical data regarding the uranium concentration in mine water and the volume of removed water is presented in Fig. 1. Water has been pumped out from two levels (6th and 11th). It can be seen that the uranium concentration of water reaches 7-10 mg/l, the removed volume of water varies between 2.5–3.5 thousand m³ per day. The elevated volume of water in the last years is due to the rehabilitation works carried out in the immediate vicinity of the mine (mine cavities has been used as a collecting reservoir for different wastewater).

TABLE I. COMPOSITION OF MINE WATER (1996-99)

pH	Na	K	Ca	Mg	Cl	SO ₄	CO ₃	HCO ₃	TDS	Unat	Ra-226
	mg/l								g/l	mg/l	x10 ⁻⁴ Bq/cm ³
7.01	430	14	180	117	174	1066	<10	794	2.44	7.73	4.38

Trace elements

Al	As	B	Ba	Mn	Si	Sr	Se	Cu	Fe
mg/l									
0.118	0.09	0.081	0.070	0.4	71	10	0.041	0.003	0.5

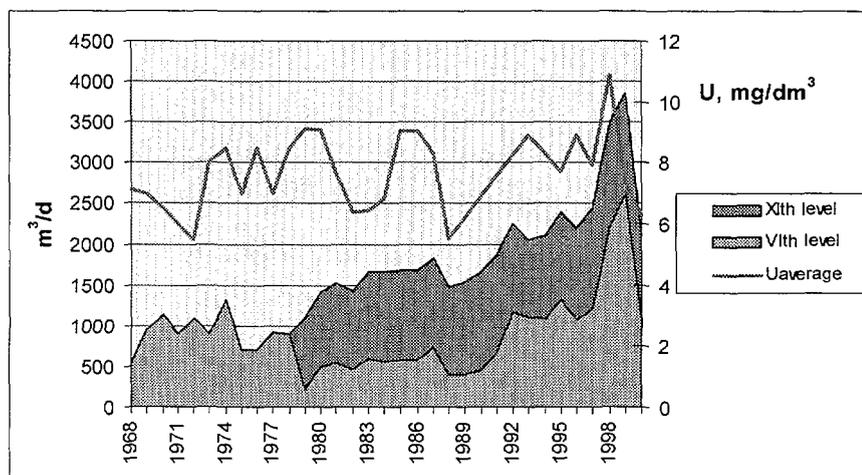


FIG. 1. Historical data.

3.1. Mine water treatment in the period of mill operation

Discharge limit for uranium is 2 mg/l. Because the uranium concentration in mine water is much higher, the uranium must be removed prior to discharge the water into the receiver.

Taking into account the composition of the water, anion exchange method was chosen the treatment. In the mill process Hungarian made anion-exchange resin Varion AP (with pyridine active group) has been used, that is why this type of resin was selected for mine water treatment as well.

For water treatment nine ion-exchange columns (each of them contains 10 m³ of ion-exchanger) were built on shaft site, from which 6 or 7 of them were in operation. The loaded resin (10-12 gU/l) was transported to a central regeneration station for removing of the uranium. With 1 m³ of resin approximately 1500 m³ mine water was treated.

Regeneration was carried out by sodium-chloride solution (80 g/dm³) containing sodium carbonate (5 g/dm³). Pregnant solution (10-12 gU/l) was further processed in the mill.

Effectiveness of the ion exchange treatment plant is shown in Figure 2, where the concentration of uranium in the mine water and treated water is presented for the last five years.

It can be seen that the uranium concentration of the treated water decreased very below discharge limit reaching in average 0,7 mgU/l.

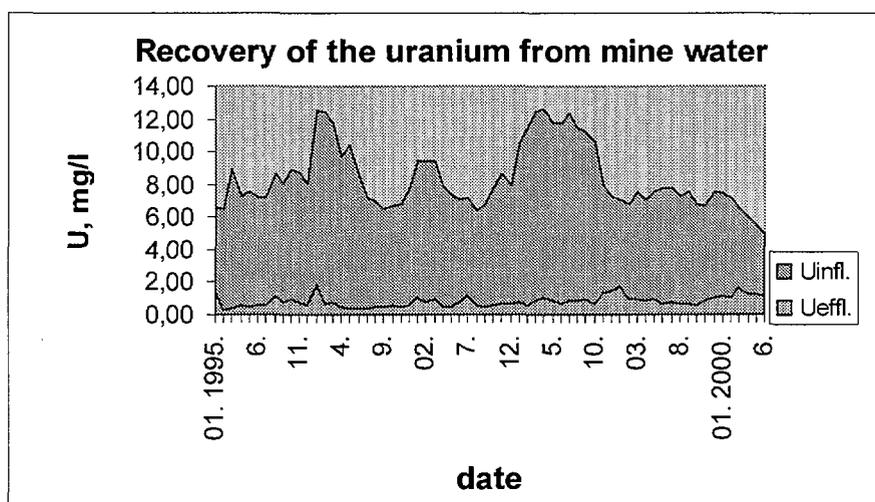


FIG. 2. Recovery of the uranium from mine water.

It is worth to mention that approximately 27 million m³ of mine water was pumped out up to now and almost 150 t of uranium was removed from the mine water of the shaft.

3.2. Mine water treatment in the post closing period

By terminating the uranium mining the mine water from the shaft No. 1 must be furthermore removed because of high uranium concentration and the above-mentioned hydrological situation. Different options were considered for water treatment for the post-closing period. After all it was decided to keep the same ion exchange process for the water treatment that had been used in the mining period. Reason of that was the still high uranium concentration of mine water.

So for the post-closing period mine water treatment is based on the removal of the uranium by anion exchange process, elution of the loaded resin by sodium-chloride solution containing some g/l of sodium carbonate.

For the further processing of eluate two possible options were evaluated:

- to precipitate the uranium and solidifying and depositing it as a waste,
- to remove the uranium in form of commercial yellow cake.

Taking into account first of all environmental considerations priority was given to the latest option, that is to removal of uranium in form of commercial by-product.

As a matter of fact the ion exchange process is well known for the company so first of all the chemical processes of the further handling of the elutes had to be more deeply investigated and developed.

Precipitation of uranium in the mill earlier was carried out by lime milk. This process has some advantage comparing it with other processes (cheap, environmentally acceptable) but the quality of the yellow cake obtained by this method does not meet the specification requirements of the converters. Therefore a new yellow cake technology had to be developed.

Developing the new water treatment technology some investigations were carried out.

Changing of the pH of the mine water

For having more detail information about the water treatment process the change of the pH of water on different steps of ion-exchange process was investigated. It was observed that the pH of water was increasing during the process. Results of the observation for a given period are presented in Figure 4, where the pH of the original mine water and that of the water living the ion-exchange process are given. The data show that the pH of the original mine water is a little below 7, but during the ion exchange process its value is increasing approximately to 7.3.

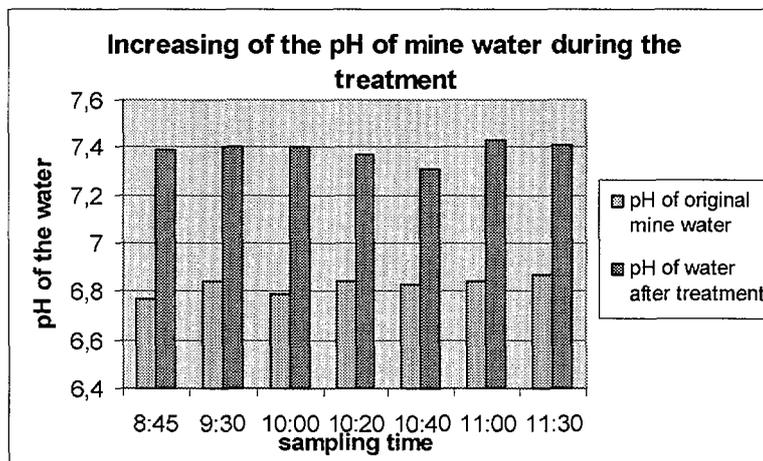


FIG. 3. Increase of the pH of mine water during the treatment.

Precipitate formation during the ion-exchange process

The mine water treatment process is simple but one operation problem should be pointed out. During whole 32 years period of mine water treatment it has been observed a brownish precipitate formation in the treatment system. The precipitate accumulated first of all in the ion-exchange resin bed and on the drainage filter elements. Composition of the precipitate is presented in table Y for main components. It can be seen that the main components are calcium, iron and manganese with an elevated concentration of uranium and arsenic.

TABLE II: AVERAGE COMPOSITION OF THE PRECIPITATE

Component	SiO ₂	CaO	MgO	Fe ₂ O ₃
concentration,	8,8-12,9	8,7-21	0,8	6,7-17,4
	MnO	As ₂ O ₃	U	
	3,45-7,1	0,031-0,078	0,1-0,4	

Investigating the origin of the main components and the elevated arsenic and uranium concentration in the precipitate we come to the conclusion that the precipitate formation in the column is likely connected with the corrosion process in the ion exchange columns and other equipment made of steel.

Uranium is reduced by the zero valent iron and than precipitates. Arsenic also can be reduced and than precipitates by iron corrosion compounds.

This observation sows the importance of the using of corrosion-resistive construction material even when the mine water has pH near to neutral.

Other conclusion that the precipitate formed during the ion exchange process has to be carefully analysed for heavy and toxic metals because these elements can be accumulated in the precipitate even if their content in the mine water is low.

Precipitation of uranium peroxide

One of the key points was the selection of the precipitant for precipitation of uranium from the eluates composition of which is presented in table 3. Investigating different agents after all hydrogen peroxide was selected which precipitate the uranium in form of peroxide:

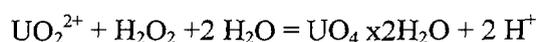


TABLE III. COMPOSITION OF THE ELUATE

Component	Concentration g/l
Uranium	10-12
Chloride	14-21
Sulphate	30-40
Sodium bycarbonate	30-40
Sodium carbonate	3-5
pH	8,5-9

Investigating the hydrogen peroxide process it was found that the carbonate complexes of the uranium must be decomposed prior to the precipitation of uranium. For this the eluates have to be acidified by sulphuric ore hydrochloric acid, presumably to pH<3. This operation should be carried out carefully to avoid the foam formation. The pH value of 3.2-3.5 should be maintained during the precipitation by adding sodium hydroxide.

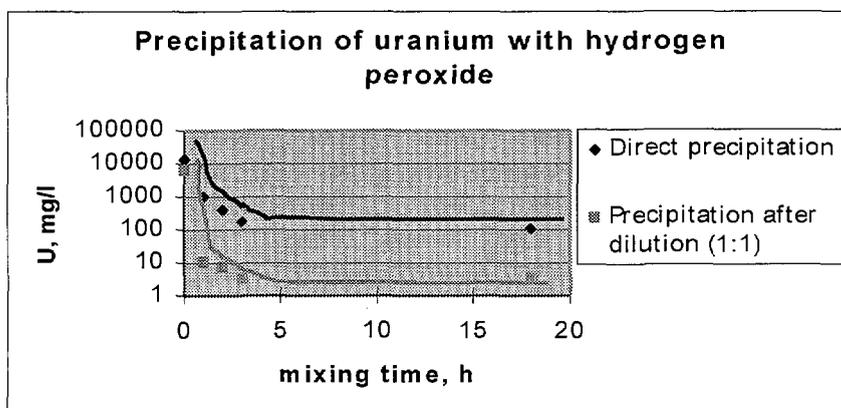


FIG. 4. Precipitation of uranium with hydrogen peroxide.

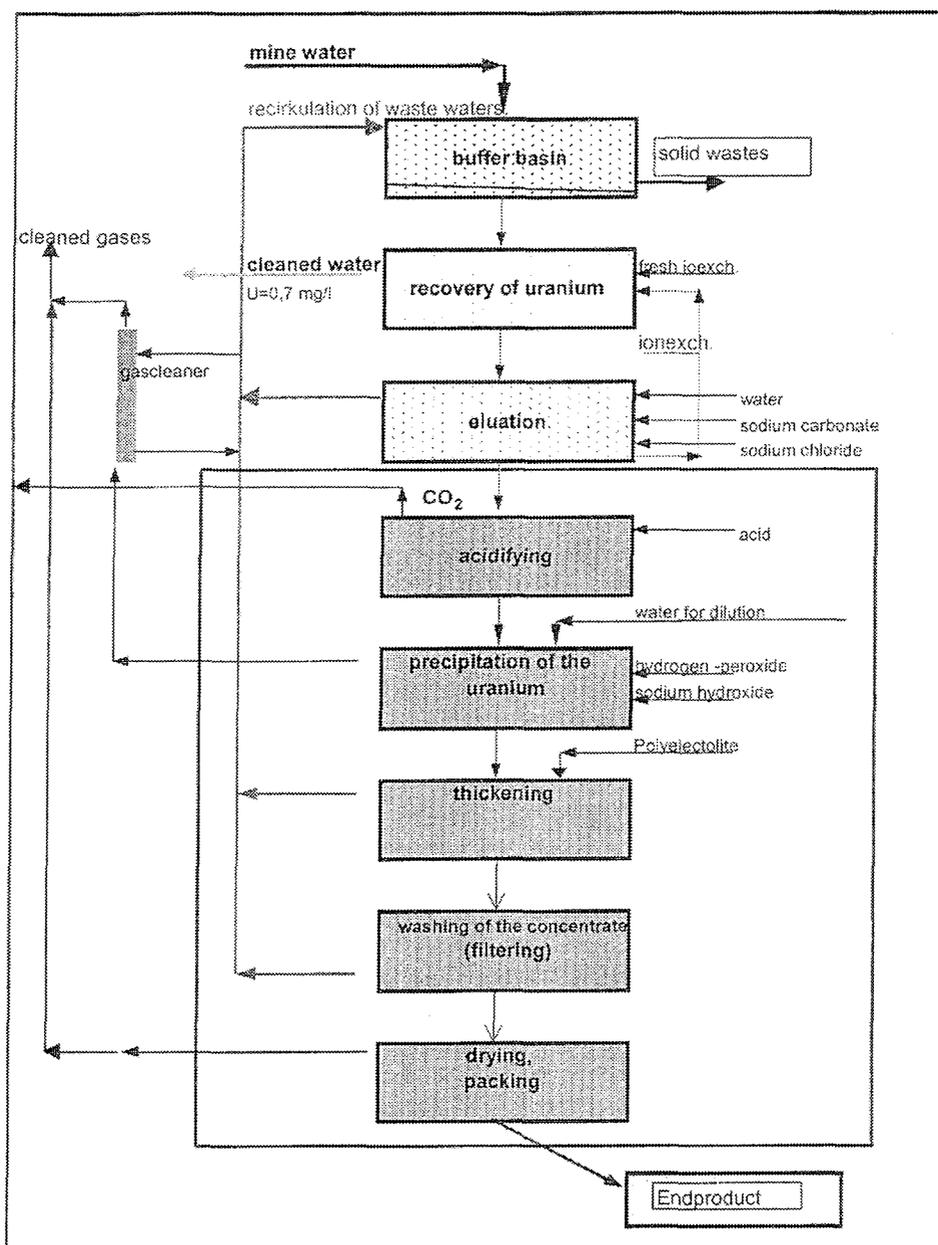


FIG. 5. Mine water treatment (main process units).

It was observed that the acidified eluates should be diluted with water for more complete precipitation of the uranium. Experimental data presented in fig. 4 show that the remained uranium concentration in the mother liquor is much less if the solution is diluted prior to the precipitation of uranium. These results can be explained also by complex formation of uranium with ligands (sulphate, chloride) present in the technological solution.

It should be mentioned that the hydrogen peroxide in the experiments was used in 20% excess to the theoretically needed value.

The precipitation in industrial scale should be carried out at ambient temperature, in continuous mood using four mixing reactors with 3-4 hours retention time and at pH 3.2-3.5.

On the bases of above-mentioned considerations and experimental results principal flow sheet of mine water treatment process was compiled. The process consists of the following main steps.

- Elevating the mine water to the surface by pumping (~110 m)
- Collecting the mine water in basin
- Uranium removal using Varion AP (Hungarian made pyridine-basic) anion exchange resin
- Elution of the loaded resin with sodium chloride solution (80 g/l) containing sodium carbonate (5 g/l)
- Acidifying the eluate for decomposing the carbonate complexes
- Dilution of the solution by water (1:1) Precipitation of the uranium with hydrogen peroxide
- Thickening of the precipitate
- Washing the concentrate for reducing the chloride, sulphate and other impurities
- Drying
- Packing the concentrate into standard drums.

The principal flow sheet of the process is presented in Figure 5.

On the bases of the above-mentioned principal flow sheet a new mine water plant has been built in this year. The plant is suitable for treatment 1.5 million m³ mine water annually. It is expected that approximately 5-7 t of uranium in form of commercial yellow cake will be obtained as a by product during the water treatment. Composition of the uranium concentrate obtained by the precipitation using hydrogen peroxide meets all standard specifications of the converters. This is due to the low pH of the precipitation (pH 3.2-3.5) and the composition of original eluates.

Uranium content of the dried concentrate is expected to be on the level of 70%.

In Table 4 the planned specific consumption of the different material used in the process are presented.

TABLE IV. SPECIFIC CONSUMPTION OF THE REAGENTS

Reagent	Concentration	Volume /kg U	Remark
Hydrogen peroxide	30%	0.55 l	for precipitation
Acid (HCl)	365 g/l	4.2 l	for decomposing the carbonate complexes
Sodium hydroxide	66 g/l	5.3 l	for pH adjusting
Polielectrolite	3 g/l	0.1 l	for thickening
Anti-foam additive	1 g/l	0.1 l	for decreasing the foam formation

4. CONCLUSION

- Anion exchange process has proved to be very effective for uranium removal from mine water.
- Uranium can be precipitated by hydrogen peroxide if the alkaline eluates are prior neutralised for decomposing the carbonate complexes.

- The effectiveness of precipitation of uranium by hydrogen peroxide is higher if the eluates are prior diluted with water.
- Precipitate formation during the ion-exchange process is likely due first of all to the corrosion process.
- On the bases of the research and development work a new mine water treatment plant is under construction with capacity of 1.5 million m³ /a of water.