MINE WATER TREATMENT (Anion-exchange and membrane processes)

I. Benkovics- J. Csicsák- Dr. M. Csővári- Zs. Lendvai- J. Molnár

Mecsek Ore Mining Company
Hungary
7633 Pécs, Esztergár L. u. 19

SUMMARY

The paper give brief overview of mining and processing of uranium ore in Hungary, Mecsek Ore Mining Company. There are information about the waste waters their chemistry and supposed volume after shut down the mining and processing activity. Process of mine water treatment is described . Results of treatment of mine water by membrane processes are presented. It is shown that using nanofiltration water with salinity of 0.7-1 g/l can be obtained from mine water (main ions are chloride and sodium) with TDS= 2-3 g/dm^3 while using reverse osmosis water with specific conductivity 50-100 S/cm can be produced in one step. The pilot scale tests have shown that uranium and radium are concentrated in retentate very effectively. This fact can give an additional possibility for decreasing the release of these radionuclides into aquatic environment (rivers, creaks, canals etc.)

HISTORICAL OVERVIEW

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 (Hungarian name of the company ***Bauxitbánya Vállalat***) in 1955, later in 1956 name of the Company was changed to ***Pécsi Uránbánya Vállalat*** and - after building the mill - from 1964 Company received its last, today's name, ***Mecseki Ércbányászati Vállalat (Hungarian abbreviation MÉV,*** **Mecsek Ore Mining Company, hereafter MEV)**. Mining claim area is 65 km^2.

In 1990-92 the Company was reorganised into some smaller limited companies. One of them is **MECSEKURAN Ltd which is responsible for the mining and processing of uranium ore** this time. Because of high production cost, the Government has decided to shut down the mines and the mill so **the mining and processing of uranium ore will be finished in Hungary at the end of this year.**

GENERAL FLOW SHEET OF THE PROCESSING OF URANIUM ORE

General flow sheet of the processing of mined out rock is shown on the **fig. 1**.

During operation period about **45 million tons of rock has been removed from 5 shafts situated on the same mining district**, two of them are still in operation, three were exhausted and closed earlier.

From 45 million tonnes of mined out rock **18 million tonnes** as **waste rock** (U< 100 g/t) was placed on 10 waste rock piles (some of them are small while three are bigger), **7.2 million** tons of low-grade ore (U=100-300 g/t, in average 136 g/t) after crushing to -30 mm has been treated by alkaline **heap leaching** on isolated area on sites near the mill. Almost **19 million tons** of ore (U=1000 g/t) has been processed **in the conventional mill built in 1962**, using sulphuric acid for leaching. A little more than **1 million tons of ore** was transported directly to the former Soviet Union in period 1958-64. Mining operation was connected with mine water removing volume of which amounted to 64 million m^3 from which during the processing of the ore in the mill about **30 million m^3** has been used. So about **34 million m^3** of mine water has been realised in the environment directly.

The neutralised waste pulp from the mill has been pumped to the tailings ponds (**two tailings ponds** were built). Total uranium production is a little more than 20 thousand tons, including the uranium exported in form of ore.

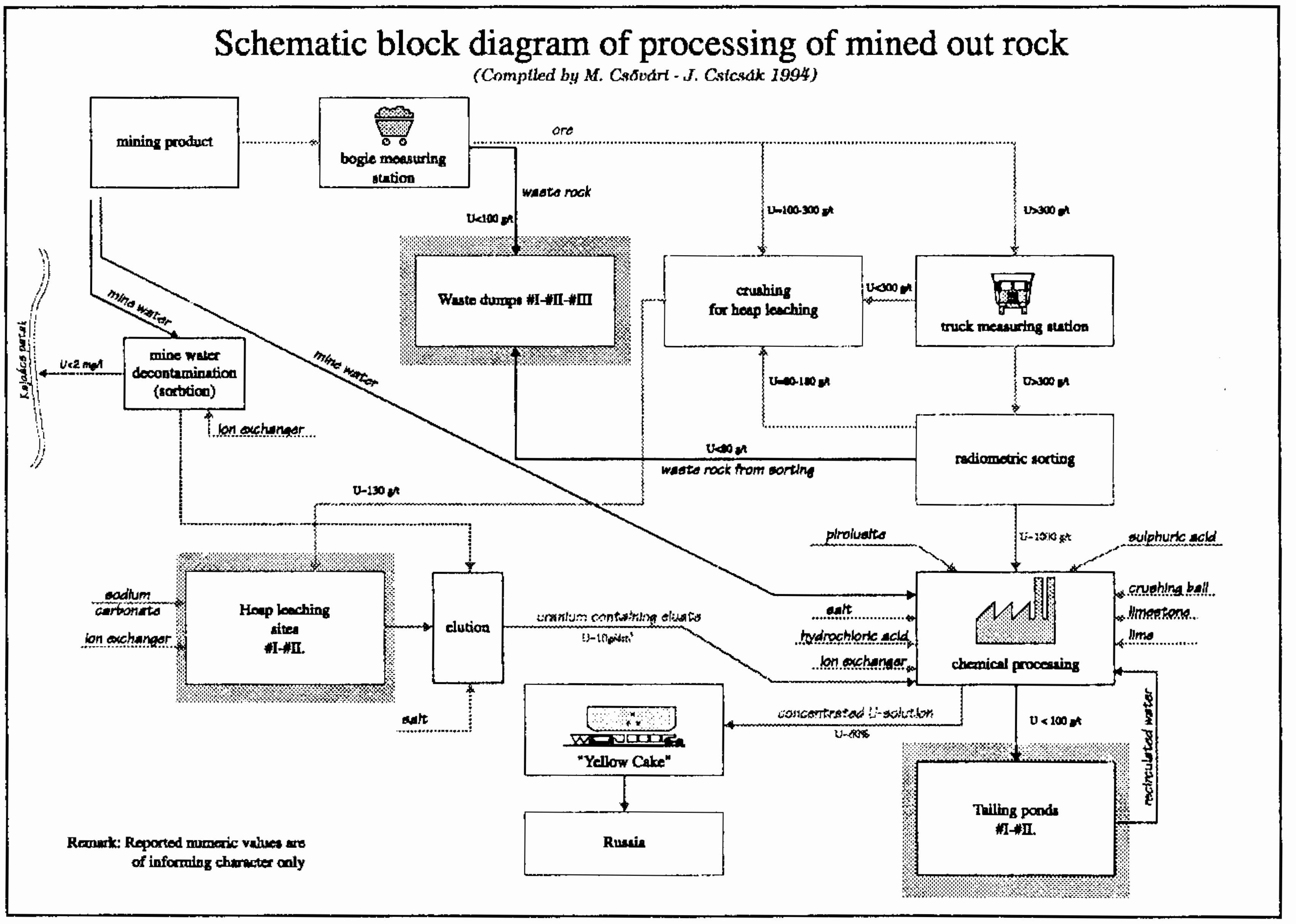


Fig. 1.

Water treatment in the past consisted of :

- **removing of uranium from part of mine water (water from mine N°I),**
- **neutralisation of barren pulp in the mill** to pH = 7-8 (from 1992 to pH = 10,5).

Bellow the mine water treatment process will be described more detail.

Mine water treatment in the past

Mine waters originate from **active** mines and abandoned ones. These waters have **low salinity** (TDS=1.5-3 g/dm^3) **and medium or high uranium content** (U=1-10 mg/dm^3). Uranium concentration of water in active mines is **only 1-2 mg/dm^3**, while in water of **abandoned ones it reaches 7-10 mg/dm^3**. As one of the abandoned mines, **mine N°I**, is in hydraulic connection with drinking water area, water **contaminated by uranium** has been pumping out from this mine from beginning 1968 to protect the drinking water aquifer. The mine water is treated by ion-exchange resin for removing the uranium (the limit for discharge: U<**2 mg/dm^3**). For treatment the same ion-exchange resin has been used as in the mill: **Varion AP (pyridine-base anion-exchanger)**.

For water treatment **nine ion-exchange columns** (each of them contains 10 m^3 of ion-exchanger) ware built 6 or 7 of them are in operation. The loaded resin (10-12 g of uranium per litre) is transported to a central regeneration station for removing of the uranium. By 1 m^3 resin approximately 1500 m^3 mine water is treated. Water treatment station is shown on **fig. 2**.

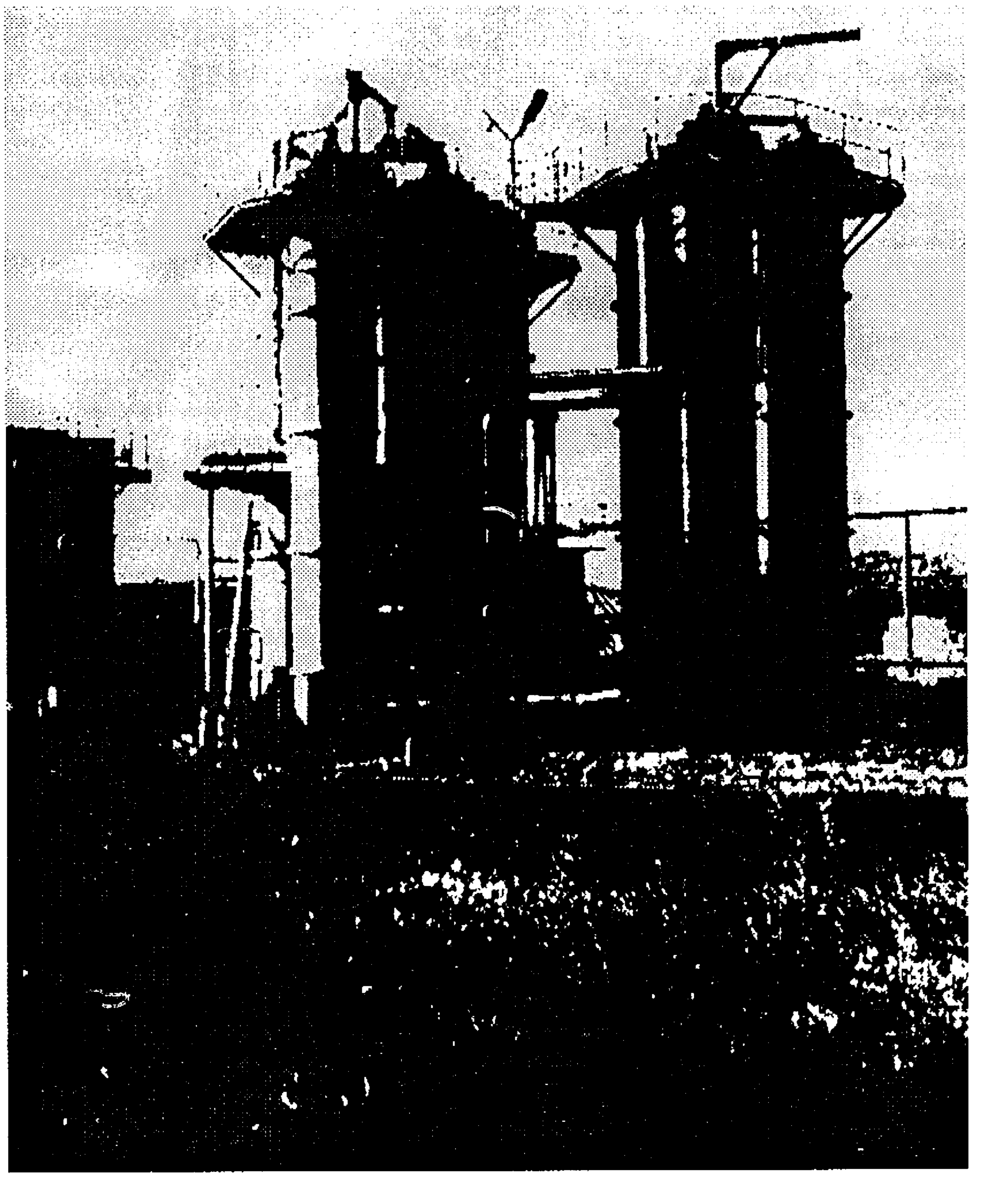


Fig. 2. : Station for recovery of uranium from mine water

The station is capable for treating 900 thousand m^3 of mine water. The loaded anion exchange resin is regenerated in the mill site. Annually approximately 5 tonnes of uranium is recovered from mine water. Uranium concentracion in treated water is 0.2 – 0.7 mg/l.

Regeneration is carried out by sodium-chloride solution (80 g/dm^3) containing sodium-carbonate (5 g/dm^3). Pregnant solution contains 10-12 g of uranium per litre. This solution is processed further **in the mill**. From mine water **about 105 tons of uranium has been recovered in period 1968-96 from the treated mine water.** Without water treatment this amount of uranium would have been dispersed in the environment.

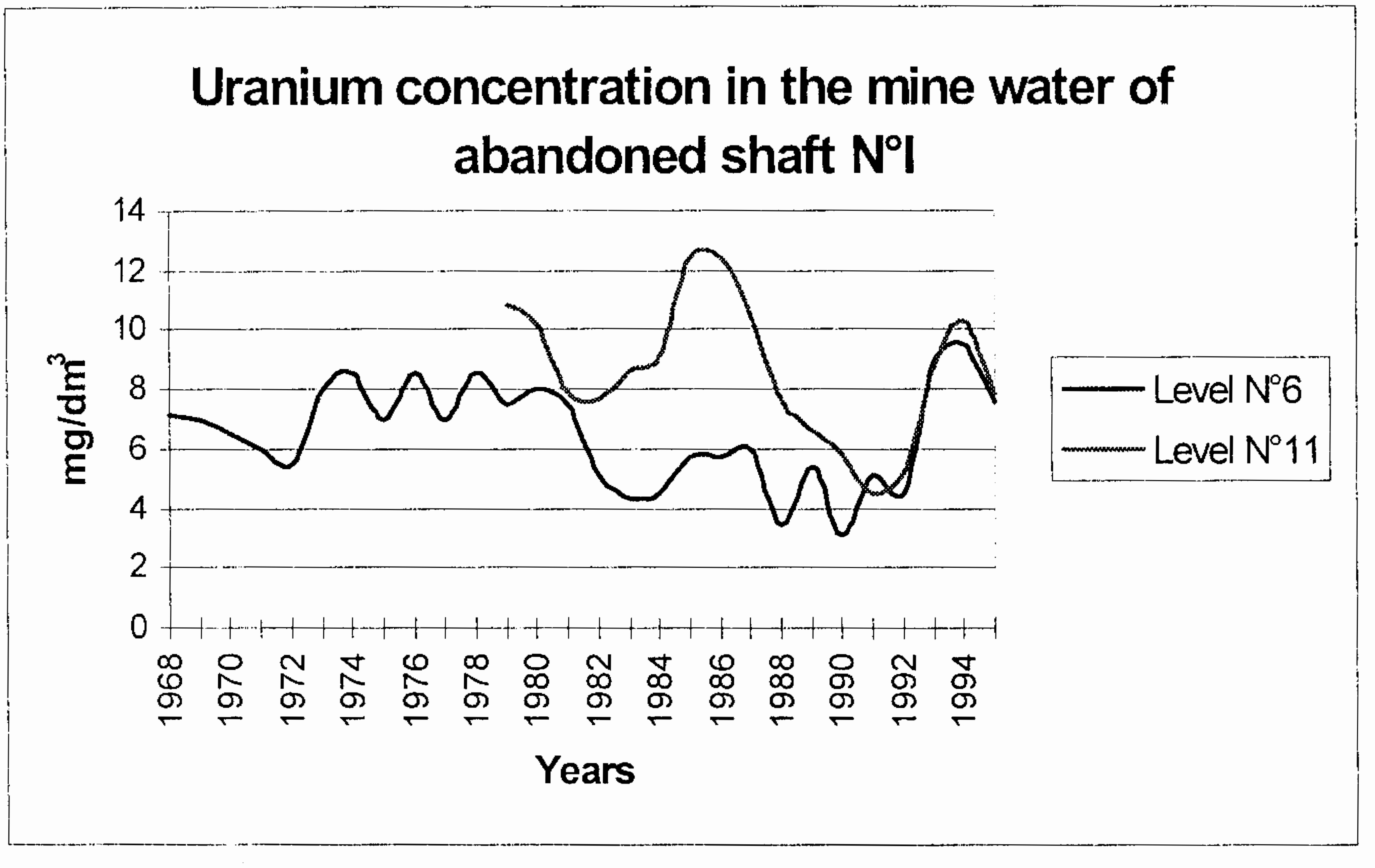


Figure 3

Uranium concentration in the treated water decreases below **0,2-0,7 mg/dm^3.**
Main technological units of water treatment are:

- pumps;
- basin for decomposition of hydrocarbonates.

As the uranium content of water from active mines is low it hasn't been treated.

CHEMISTRY OF MINE WATER AND OT HER EFFLUENTS AND THEIR VOLUME IN THE NEAR FUTURE

By shut down of the mining and processing of uranium ore some changes are foreseen in water treatment. Approximate composition of waters of different origin (from different objects) is presented in table 1. It can be seen that some effluents are contaminated either by radium or uranium or by high TDS. **Discharge limit for the Company: Ra < 1,1 Bq/dm^3, U < 2 mg/dm^3.** It is supposed that the volume and most important pollutants to be about the value presented on fig. 4 and 5.

Estimation of the volume and composition of effluents for the future

Volume of effluents

Estimations are based partly on available data **from the experience in the past** and hydrologic observations (mine water, seepage water) partly **from actual measurements** (free waters on heap leaching area, tailings ponds) partly **from planed activity** (groundwater restoration, covering). Main uncertainty is the flooding rate of abandoned mines but this process will probably lasted more than 20 years so at this moment the flooding rate is not so important.

Composition of effluents

This task is rather difficult first of all because large area will be disturbed by reclamation woks. Reclamation activity usually led to relocation already consolidated wastes and formation new surface. Due to this facts some **increasing of the uranium concentration** in waters is likely in first period after remediation. This question may be important when seepage from waste rock pile is significant. In our case this problem is only of minor importance as the waste rock piles are situated above shaft which collects most part of seepages.

Estimation of uranium content in mine water is an other problem. As in our case this figure affect considerably the average uranium concentration of the water to be treated it is important to know the real value of that. In this case **extrapolation** was made using data from the past 28 years (uranium concentration of mine water from shaft N°I). Taking into account these data it is likely that **uranium concentration** will slightly dropped in the next ten years but remains still **above 2 mg/dm^3** (discharge limit for the company).

Estimation of radium concentration is based on historic data of radium concentration in waste water of different origin. In this respect it should be mentioned that only tailings water and process water from heap leaching showed elevated radium-226 concentration (>1 Bq/dm^3) in the past. There is no reason for significant changing of these values in the future.

Estimations of TDS in the case of mine water and seepage waters from waste rock piles are based again mainly on historical data. As the sulphide content of the host rock is low (0,2-0,4%) it is unlikely that the TDS of the effluents will be much higher than today even after relocation some part of wastes, nevertheless some increasing of this value may take place in the first years of remediation. Generally it can be given an **approach** that in this respect no changes can be expected. In the case of groundwater to be treated MEV also has problem because this variable will depend in large extent from different hydrological facts unknown today. Certain estimation can be based on the data from monitoring wells and the water flow data of the area. In any case the estimation should be improved every year taking into account the latest data.

Based on the above mentioned principles, estimation of the volume and composition (in regard to uranium, radium, TDS) of effluents from different sources are given on fig. 4 and 5**for a ten years period.** Main data for resulting mixed water are presented in the table 2 as well. In the table the quantity of component in question is also given. At this table groundwater restoration process is included also with pumping out 400 thousand m^3 polluted ground water per year.

Following conclusions from the data presented can be drown :

- uranium concentration in **collected effluent** is higher than **2 mg/dm^3** (maximum: 4,6 minimum: 2,98 mg/dm^3);

- radium concentration of **collected effluent** is on the level of **1 Bq/dm^3**. Main source of radium-226 is the tailings free water, for this - after discharging of free water from tailings ponds, this value **will decrease to 0,54 Bq/dm^3**;
- **dissolved solids (TDS)** are higher **(**maximum: **5,43** minimum: **4,41 g/dm^3)** than the limit for discharge (the limit is **2 g/dm^3** this time), main source of that are tailings waters;
- **total volume** of collected effluent reaches **a pick: 2,734 thousand m^3 in 1998, but than decreases to 1542 thousand m^3 and will remain on this level presumably in long period.** This volume includes 400 thousand m^3 of removed polluted groundwater from the vicinity of tailings ponds.

Without entering in detail it can be mentioned that the high volume of discharged water in period of shut down the mines is connected with discharging the free water from heap leaching piles and tailings pond.

Composition of effluents and their volume in 1996

Table 1

Component	Conc.	Mines			Waste rock pile			Heap leaching			Tailings ponds			
		Water from shaft N° I	Water from shaft N° III	Water from North and East tunels	Seapage water from pile N° I	Seapage water from pile N° II	Seapage water from pile N° III	Free water	Water after washing of heaps	Seapage water	Free water	Seapage water	Water removed*	Removed water after treatment with lime**
Na	mg/dm^3	582	110	19	100	87	136	4963	3120	3429	931	766	884	884
K	mg/dm^3	12	10	7	15	13	14	37	10	10	148	140	24	<5
Ca	mg/dm^3	222	152	108	216	287	177	10	3	5	576	472	624	820
Mg	mg/dm^3	146	80	66	122	162	92	32	28	25	1232	2093	1364	77
Cl	mg/dm^3	250	20	28	65	45	50	1100	924	824	2113	1503	1623	1623
SO_4	mg/dm^3	1272	567	220	827	999	676	6018	3470	3580	5721	9436	5913	1902
CO_3	mg/dm^3	0	0	0	0	0	0	728	210	525	<10	<10	<10	<10
HCO_3	mg/dm^3	919	401	379	374	573	400	2378	2010	2230	65	167	812	0
TDS	g/l	2,94	1,15	0,651	1,56	1,89	1,36	14,07	8,76	9,49	10,83	14,56	10,86	5,33
Bicarbonate hardness	n°	42,2	18,4	17,4	17,2	26,3	18,4	109,2	92,3	102,4	3,0	7,7	37,3	0,0
Total hardness	n°	64,7	39,7	30,3	58,3	77,5	45,0	8,8	6,9	6,5	364,3	548,0	401,4	132,5
PH		8	8,2	7,3	7,8	7,8	7,9	8,9	8,5	8,5	7,2	7,2	7,3	10,2
U	mg/dm^3	7,5	1,4	0,7	9,5	27	3	5	3	15	0,03	0,03	0,03	0,01
Spec. conductivity	µS/cm	4140	1816	816	2437	3777	2250	19615	11350	11350	12350	19470	14530	
Mn	mg/dm^3										180	250	0,36	0,1
Ra-226	Bq/dm^3	0,6	0,6	0,6	0,09	0,14	0,02	1,5	1,5	1,5	6,36*	10,98*	0,08	0,08
NH_4	mg/dm^3	0,31	0,03	0,02	0,01	0,01	0,01	0			5,69	5,9		
NO_3	mg/dm^3	7,2	13	16	18	18	18	8,3			78	56	21	21
NO_2	mg/dm^3	0,11	0,05	0,03	0,01			0,015			5,4	1,78		
Volume of water discharged in 1995***	10^3 m^3	700	450	200	32	32	120	50****	-	-	-	-	-	-

Remark: * contaminated ground water, removing is scheduled from second half of 1996
** soppoused composition after treatment by lime milk
*** dischaged after removal of uranium
**** over balance

Mine water treatment in next years

As the waters have to be released to the environment, it necessary to treat some of them: partly for reducing the salinity and radium, partly for removing the uranium. The main water treatment issues will be:

- treatment of free water from tailings pond and heap leach piles has to be discharged after partial desalination and radium removal (using lime and barium-chloride);
- in connection of ground water contamination on tailings ponds site, ground water restoration process is to be organised (by removing the polluted water and injection clean water);
- mines will be flooded with the exception of mine N°I from which mine water has to be pumped on the surface and treated for removing of uranium.

Mixed water from all sources
Table 2

			YEAR											
			1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007
Volume	V	th m^3	1784	2234	2734	2234	1832	1542	1542	1542	1542	1542	1542	1542
Uranium	U	mg/l	**4,60**	**3,93**	**3,35**	**3,77**	**3,73**	**3,72**	**2,98**	**2,98**	**2,98**	**2,98**	**2,98**	**2,98**
		kg	8209	8768	9155	8425	6834	5736	4592	4592	4592	4592	4592	4592
Radium	Ra	Bq/l	**0,70**	**0,84**	**1,05**	**1,07**	**1,10**	**0,55**	**0,54**	**0,54**	**0,54**	**0,54**	**0,54**	**0,54**
		kBq	1342	1887	2867	2387	2014	844	830	830	830	830	830	830
Salinity	TDS	g/l	**3,30**	**4,98**	**5,10**	**4,86**	**5,43**	**4,54**	**4,51**	**4,41**	**4,41**	**4,41**	**4,41**	**4,41**
		t	5879	11129	13939	10849	9955	7005	6949	6799	6799	6799	6799	6799

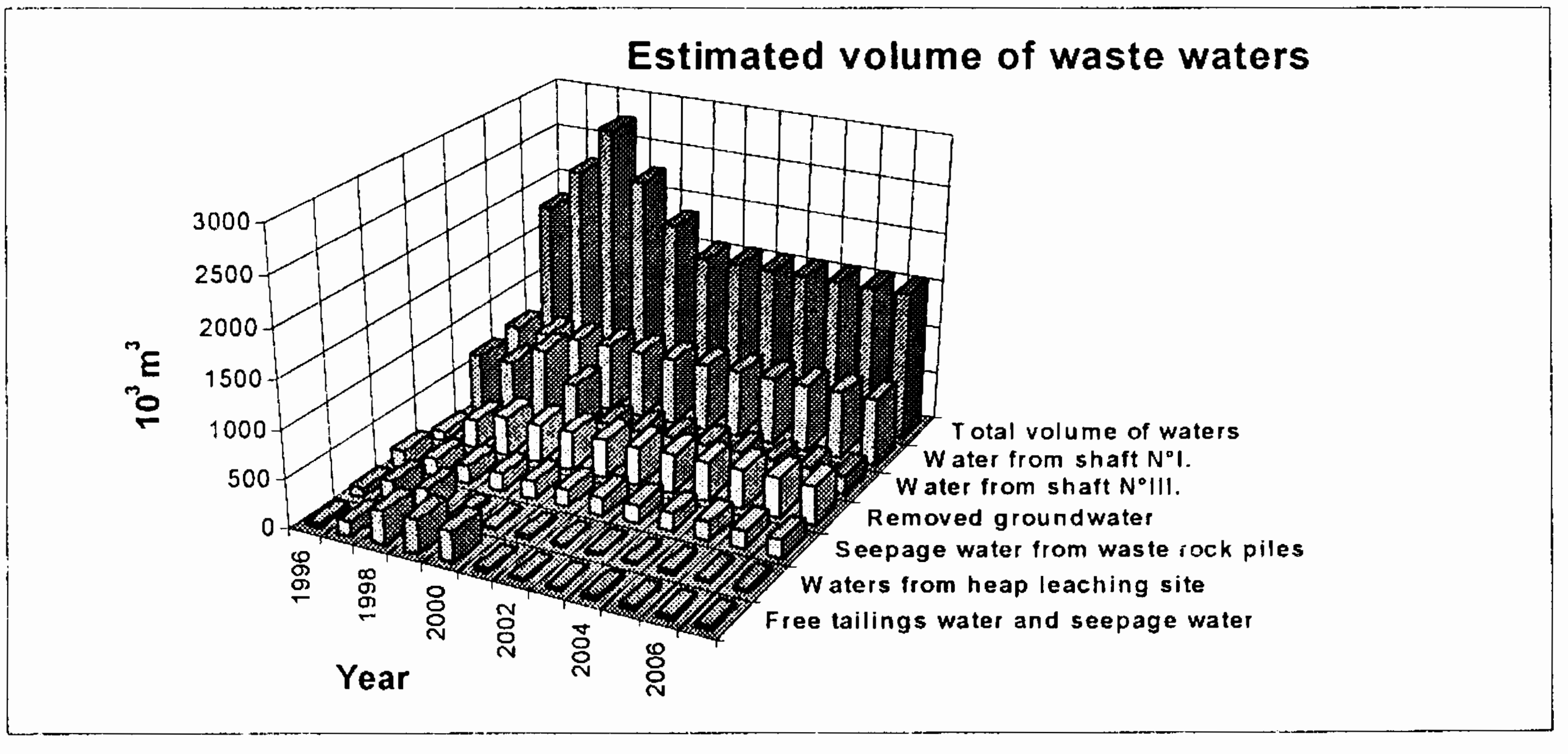


Fig. 4

In this paper treatment of mine water is discussed only.

Removing of uranium

Mine water is supposed to be treated for removing of uranium. This process essentially will be the same as it is used nowadays, that is ion-exchange process in the above described columns. The removed uranium than will be processed to yellow cake. It is supposed that about 5-8 t U/a will be obtained from water treatment process. Cost of treatment is planed to be around 0.3-0.5 US$/m^3 of treated mine water including the pumping cost.

Membrane processes

In co-operation **with UWATECH - ROPUR Ltd** (German company) some pilot scale tests were carried out by using reverse osmosis and nanofiltration for cleaning mine water from radionuclides and different chemicals. The reason of these experiments were to show that water appropriate quality can be obtained from mine water if above mentioned ground water restoration process will be connected with washing of the polluted subsoil on drinking water area and **for this clean water will be needed**.

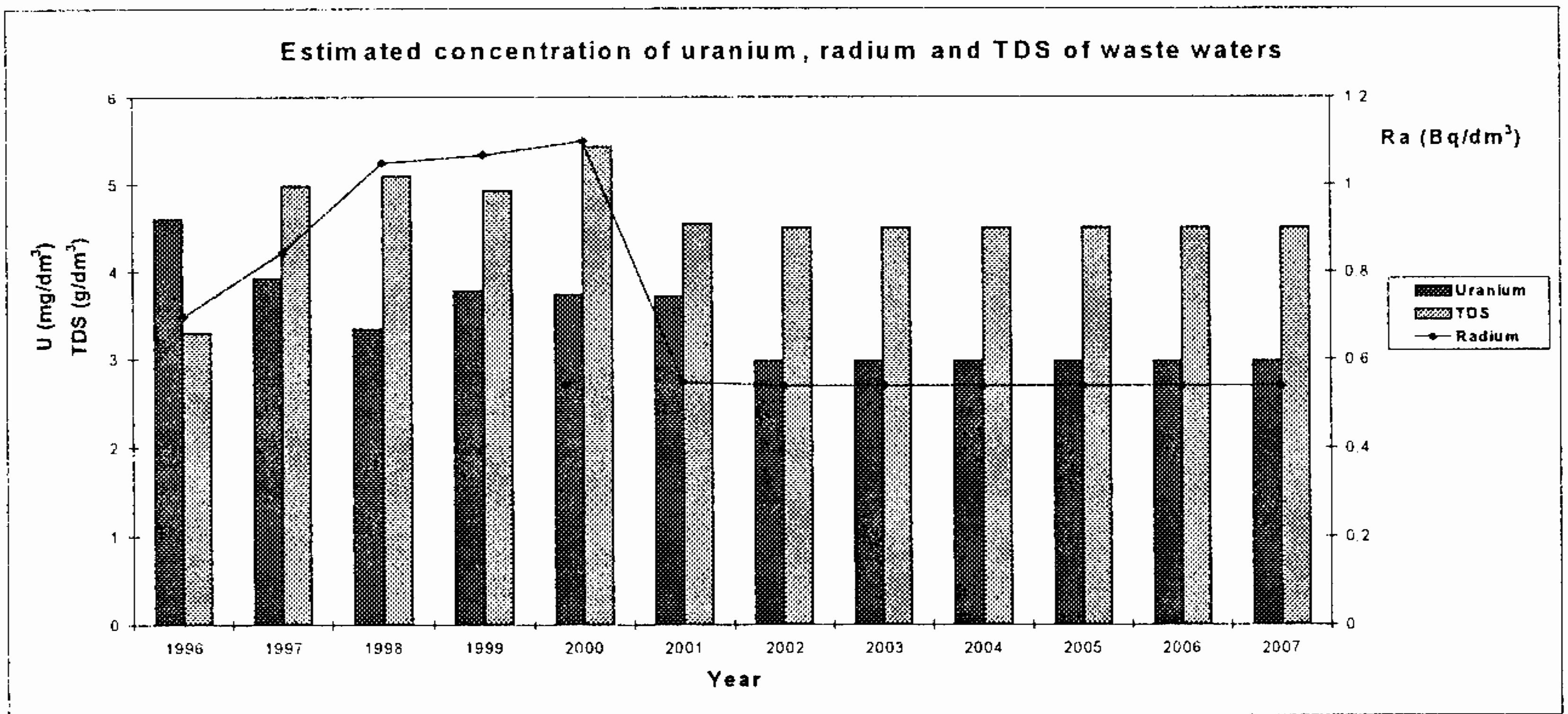
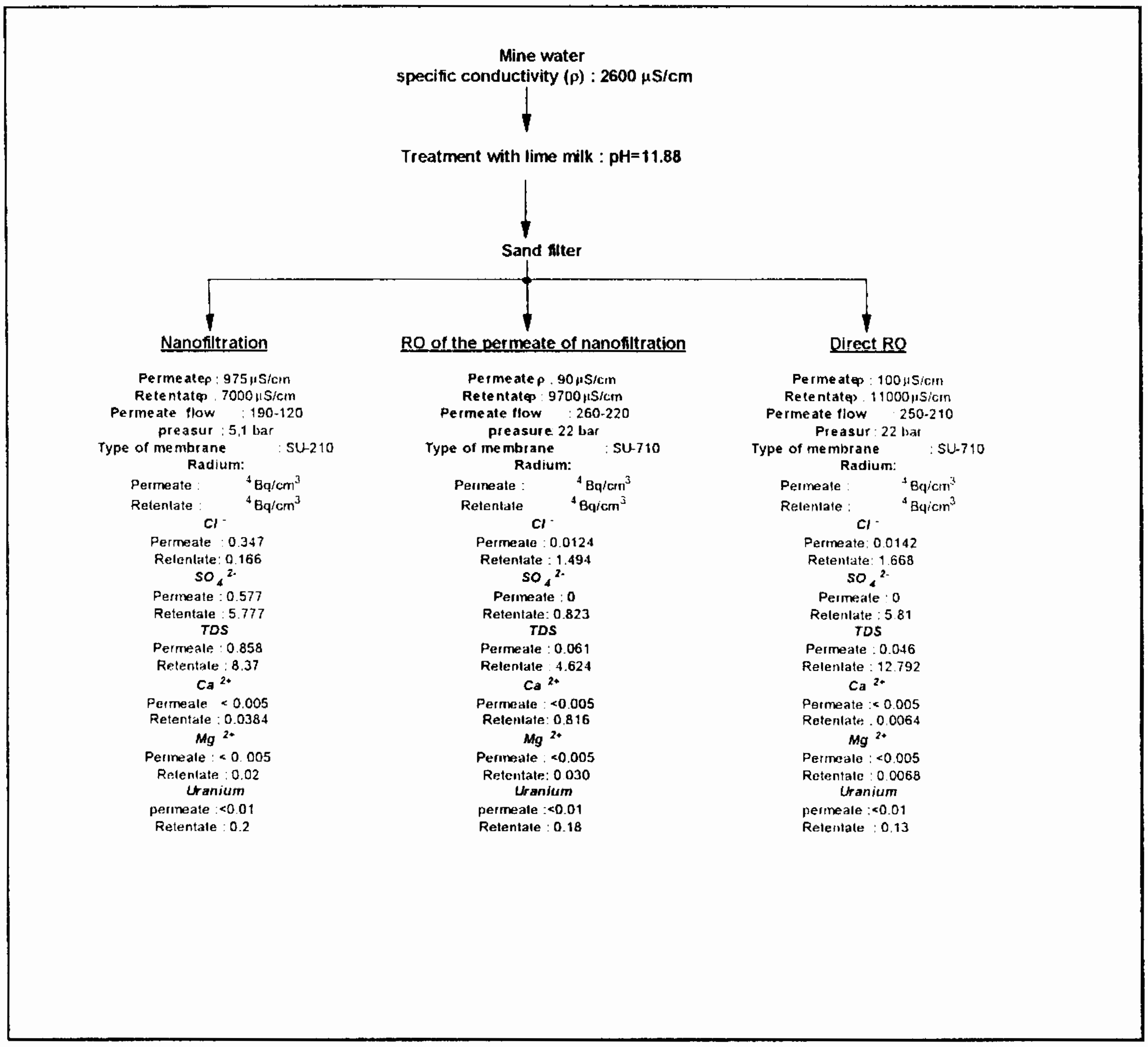


Figure 5

Experiments have been carried out not only on mine water but other waste water : water from heap leaching, tailings water etc. On figure 6 results of nanofiltration and reverse osmosis are summarised when mine water treated by ion-exchange resin was neutralised filtered by sand filter and than processed by these methods.

It can be seen that membrane processes are very effective for removing of radionuclides: uranium concentration decreases bellow 10 mg/l, radium concentration also decreases to background value in permeate. Desalination depends from the type of membrane. The quality of permeate seems to be very good so it can be used not only for washing of soil but for different other purposes, too. Of course it is possible to remove uranium and radium by further treatment of retentate substantially reducing the release of pollutants in the environment.

Implementation of membrane processes for water cleaning will depend from results of economic evaluation.



Mine water treatment by nanofiltration and revers osmosis

Figure 6

The pilot scale membrane water treatment equipment consist of prefiltration module, modules for ultrafiltration and nanofiltration as well for reverse osmosis. Maximum pressure is 70 bar, the maximum feed flow is about 1 m^3 per hour. During the tests TORAY and DESAL membrane elements were used.