Recent findings on the influence of pit waters on the shutdown of the Idrija mercury mine

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ABSTRACT
During 500 years of operation, the Idrija Mine produced approximately 145,000 tons of mercury, second only to Almaden. In 1988, a decision was made to definitely shut down the mine. Geoscience has subsequently been used to explain the structure of the deposit, mercury fluxes and speciation, and the potential influence of the mine on the biosphere, and to develop remedial measures that neutralized the harmful effects and permitted, along with reorientation into new industries, a safe, sane and sustainable living to the population. However, geochemical monitoring indicates that despite our knowledge of the geological structure and hydrological conditions, iron (Fe_{tot}), sulphate (SO_4) and mercury (Hg) concentrations in the pit water outflow increased in 1998-99.

KEY WORDS: geochemistry, hydrogeology, mine closure

INTRODUCTION
The Idrija ore deposit is situated in the town of Idrija, and extends 1500 m along a north-west/ south-east direction. It is 450 m deep and 400-600 m wide. The mine had 15 levels reaching a depth of 380 m (36 m below sea level). The complex geological structure is the consequence of several tectonic phases, which divided the original ore deposit into two major sections: the Idrija ore deposit and the Ljubevc ore deposit. The hydrogeological conditions in the Idrija ore deposit were relatively favourable until new fronts were opened and advanced in the direction of the Ljubevc ore deposit, which resulted in increased inflows of water on the XIVth level.

The shutdown of the mine is progressing gradually, from the lowest 15th level towards the surface, and is accompanied by reinforcement work, since the greater part of the mine lies directly below the town of Idrija. After the reinforcement work is completed, the flooding of this part of the pit will follow (Bajželj et al., 1996). At present, the pit is flooded up to the XIth level. The long-term programme for the gradual, complete and permanent shutdown of the Idrija Mine includes the monitoring of various aspects of already performed closure activities related to air, water, soil, and sediments (Dizdarevic and Rezun, 1998).

HYDROGEOLOGICAL CHARACTERISTICS OF THE ORE DEPOSIT

The ore deposit and its surroundings are comprised of several hydrogeological blocks and impermeable hydrogeological barriers. The hydrogeological block of the Idrija ore deposit is characterized by the presence of backfills (40% porosity) and unfilled shafts on lower levels of the ore deposiis, in addition to karst aquifers and fractured aquifers.

The impermeable barriers enclosing the old part of the Idrija ore deposit consist of Carboniferous shale below the deposit, thrust sheets along the southern edge, and a Carboniferous layer above the deposit. On the north side, the deposit is closed in by an impermeable, clayey zone of the Idrija fault.

In all aquifers, the level of ground water is above the level of the mine infrastructure. The pit waters do not supply water to any of the aquifers in the vicinity; instead water from neighbouring aquifers flows into the mine. The main inflows of water into the ore deposit occur through shafts, galleries, drilled hydrological barriers or barriers partly demolished due to excavation (Rezun and Dizdarevic, 1997).

The flooding of the ore deposit up to the IVth level (+192m) will keep pit waters within the limits of the abandoned ore deposit. The only possible source of pollution will be where the pumped pit water discharges into the above-ground water course – the Idrijca River.

FLOODING OF THE BOTTOM PART OF THE ORE DEPOSIT

Ljubevc, the part of the ore deposit that was displaced alongside the Idrija fault, has no hydrological barrier towards the surface and represents an open aquifer. In the 1970's, this part of the ore deposit was linked to an investigative shaft, which during drainage contributed most of the water that had to be pumped from the mine. In 1988, this part of the ore deposit was separated from the remainder of the deposit by closing a water gate, which reduced the water inflow into the pumping facility from the previous 36.5 L/s (mean value) to 15.0 L/s.

As both parts of the mine were flooded (1992-94), the underground water level in the Ljubevc ore deposit rose at a quicker rate than in the Idrija ore deposit. The pumps in the new pumping facility were put into operation for the first time in November 1994, when the water reached the XIth level. The water level in the ore deposit rose as predicted (Petric and Janez, 1997).

The water flowed into the Idrija ore deposit at 15-17 L/s. Inflows fluctuated in line with hydrometeorological conditions. Inflows into the ore deposit were calculated based on the total operating hours of pumps in the pumping facility on level XI, where all pit waters are collected. An unexpectedly large inflow of water into the pumping facility on level XI in 1998 caused serious difficulties, as the pump capacity of pumps was initially inadequate. Fortunately, the inflow rose gradually, allowing additional pumps to be installed, increasing the amounts of pumped water. The water inflow increased from 17 L/s (mean value) in August 1998 to 35 L/s in July 1999. Based on existing documents and the observed rhythm of fluctuations of inflows into the pumping facility, we have concluded that an uncontrolled and unexpected inflow of water from the area of the Ljubevc ore deposit occurred, probably due to the partial collapse of the Ljubevc water gate area (Rezun et al., 2001).

In addition to the increased inflows and the consequentially increased quantities of pumped out pit water, chemical analyses of the quality of pit water being discharged indicates that the water is more contaminated.

POLLUTION OF PIT WATER

In 1992, our attention was not only focused on monitoring the flooding of the ore deposit, but also on the quality of water being discharged into the Idrijca River. During the shutdown and flooding of the pit (Oct 1992 – Nov 1994), increased concentrations of Fe_{tot} and SO_4 (above the maximum allowable concentration - MAC) were found in the water being collected up to the XI^{th} level. However, the Hg concentration did not exceed MAC (Ulrich-Obal et al., 1997).

Initial analyses of the pumped water showed that the maximum concentrations allowed by Slovene standards for the discharge of technological waters were greatly exceeded, particularly in the case of iron and sulphates, due presumably to the of washing of old backfills made of smelting wastes. Within a few years (1995, 1996), iron concentrations fell below the allowable limit, while sulphates continue to remain an unsolved problem. Despite our fears, the limit value for mercury was not exceeded. In addition to samples of pumped water, water samples from the repeatedly flooded Ljubevc ore deposit have been analysed. The results are within the limits applicable for pit water, and the quality has not changed significantly since before shutdown (Rezun et al., 2001).

Monitoring the pollution of the Idrijca River by the pit water involves determining the quality of water in the Idrijca River prior to the discharge of pit water, directly at the discharge, and approximately 200 m downstream, after dilution, in conformity with applicable regulations (Figure 1). The results are presented in Tables 1, 2, and 3 as the annual mean values of monthly analyses of samples taken during the pumping of pit water (operation of pit pumps).

Figure 1. Water sampling locations in the Idrijca River (a. Idrijca River prior to discharge of pit water, b. at discharge of pit water, c. Idrijca River 200 m after discharge of pit water)

Iron (Fe_{tot})

A HACH spectrophotometer has been used for chemical analysis of the water. The total iron concentration *(Fe_{tot})* is being determined using Hach's TPTZ (2,4,6-tripyridyl-s-triazine) spectrophotometric method; ISO 6332 – spectrophotometrically with 1,10 – phenatrolin. Table 1 presents the annual mean Fe_{tot} concentrations in the Idrijca River prior to discharge, at discharge, and after the discharge of pit water. The 2003 results relate to the period from January to May inclusive*.

Sulphates (SO_4)

Sulphate ions *(SO_4^{2-})* were determined using the HACH spectrophotometric method. Table 2 presents the annual mean SO_4^{2-} concentrations in the Idrijca River prior to the discharge of polluted pit water, at discharge, and after the discharge of pit water. The 2003 results relate to the period from January to May* inclusive.

Table 1. Annual mean Fe_{tot} concentrations (mg/L) in the Idrijca River

Year	Idrijca prior to discharge X_{av}±SD		At discharge X_{av}±SD		Idrijca after discharge X_{av}±SD	
1995	0.03	0.02	4.05	2.78	0.35	0.50
1996	0.07	0.03	1.64	0.69	0.13	0.14
1997	0.04	0.03	1.16	0.35	0.06	0.03
1998	0.08	0.09	0.80	0.29	0.05	0.04
1999	**0.06**	**0.03**	**1.98**	**0.64**	**0.07**	**0.03**
2000	0.06	0.04	1.11	0.36	0.11	0.06
2001	0.06	0.04	1.44	0.49	0.07	0.05
2002	0.04	0.03	1.73	1.02	0.07	0.05
2003*	0.05	0.03	1.26	0.29	0.04	0.01
MAC			**2.00**			

Table 2. Annual mean concentrations of SO_4^{2-} (mg/L) in the Idrijca River

Year	Idrijca prior to discharge X_{av}±SD		At discharge X_{av}±SD		Idrijca after discharge X_{av}±SD	
1995	4	7	4681	2463	511	536
1996	15	27	2905	1702	322	604
1997	4	4	2736	712	48	50
1998	**4**	**3**	**3145**	**1801**	**22**	**11**
1999	4	3	1594	297	29	17
2000	8	9	888	283	22	16
2001	6	2	894	155	17	6
2002	8	1	588	222	18	8
2003*	5	3	735	277	19	4
AMAC			**1000**			

Mercury (Hg)

Total mercury (Hg_{tot}) in water has been determined according to the SIST ISO 5666-2 and SIST ISO 5666-3 standard methods. Water samples are exposed to UV rays, with an added solution of KBr and $KBrO_3$ in concentrated HCl. Table 3 presents the annual mean Hg_{tot} concentrations in the Idrijca River prior to the discharge of polluted pit water, at discharge, and after the discharge of pit water. The 2003 results are presented for the period from January to May* inclusive.

Table 3. Annual mean Hg_{tot} concentrations (ng/L) in the Idrijca River

Year	***Idrijca prior to discharge*** $X_{av}\pm SD$		***At discharge*** $X_{av}\pm SD$		***Idrijca after discharge*** $X_{av}\pm SD$	
1995	30.0	0.0	100.7	58.3	40.2	22.5
1996	70.2	67.6	125.8	104.3	67.2	57.6
1997	91.3	139.1	126.4	111.1	50.7	55.0
1998	19.1	10.3	200.6	99.0	25.8	10.0
1999	14.3	4.5	1255.5	1076.1	83.7	134.4
2000	14.9	8.1	427.9	229.3	27.8	13.1
2001	18.1	8.4	467.6	465.4	26.7	22.7
2002	34.4	23.4	427.7	367.0	61.5	67.1
2003*	45.4	31.1	285.7	146.1	86.7	47.7
MAC			**10 000.0**			

FINDINGS

Due to the repeatedly increased inflows of water from the Ljubevc deposit into the pit of the Idrija Mine in 1998 and 1999, the water pumped from the pit in this period was found to have increased concentrations of Fe_{tot}, SO_4^{2-} and Hg_{tot}. Substantially increased concentrations of sulphates were first observed in pit water in 1998 (Figure 2), followed by increased iron (exceeding the MAC) and mercury concentrations in 1999 (Figures 3, 4); SO_4^{2-} concentrations continuously exceeded the absolute maximum allowed concentrations (AMAC) for the entire monitoring period, and increased substantially in 1998. However, Hg_{tot} concentrations never exceeded the MAC values despite following similar trends to the concentrations of the other two parameters.

After 2000, the water inflows into the flooded part of the pit (pumping facility) began to stabilize due to drainage of the open aquifer above the flooded Ljubevc deposit, resulting in a gradual decrease in the concentrations of monitored quality parameters of pumped pit water. In general, the monitored elements of pit water quality are declining and attaining the values recorded before 1998.

The most probable reason for the increased concentrations of monitored parameters due to increased water inflows into the pit is believed to be the increased leaching of heavy metals from old backfills (Fe_{tot}, SO_4^{2-}) and rocks containing native mercury (most of the Hg in samples was associated with suspended particles rather than as dissolved in water). Similar findings were observed in the 1992–1995 period, when the bottom part of the pit was flooded for the first time from the XVth to the XIth levels, including the old backfills in the pit (Ulrich-Obal et al., 1997).

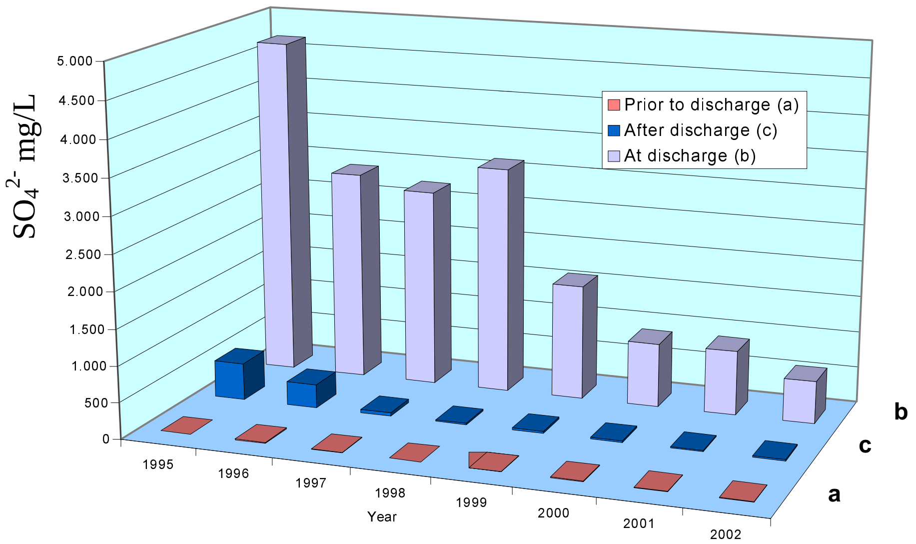

Figure 2. Average annual concentration of sulphate in water at designated sampling locations

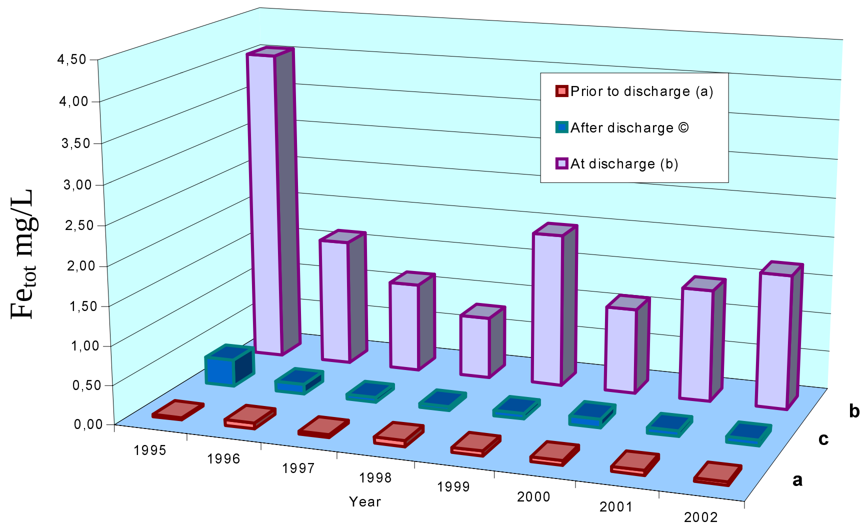

Figure 3. Average annual concentrations of iron in water at designated sampling locations

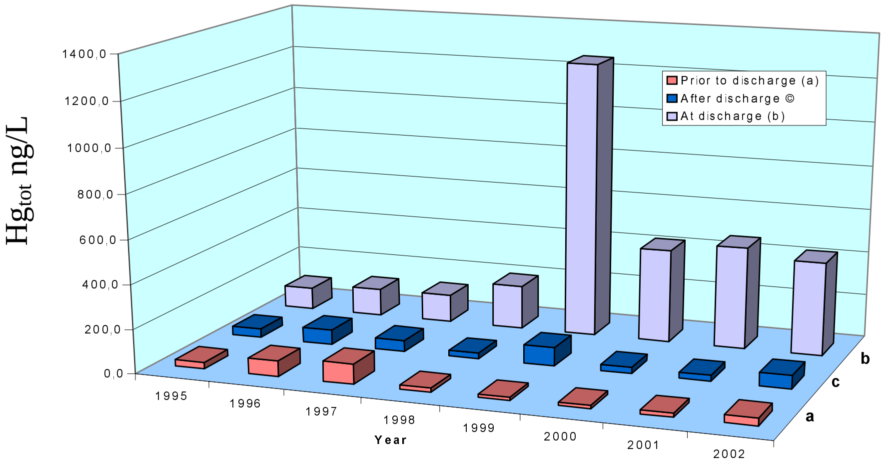

Figure 4. Average annual concentrations of mercury in water at designated sampling locations

CONCLUSIONS

The mine shutdown programme foresees, in the final phase, the flooding of the pit up to the IVth level. This may considerably worsen the situation as regards slides and shifts of rock masses above the pit, as well as the quality (Fe_{tot}, SO_4, Hg_{tot}) of discharged pit water. For this reason, the flooding of the pit will be performed gradually, the installed measuring devices and eventual movements of rock masses will be continuously monitored, and the discharged pit water analysed. The current monitoring of pit water has shown that continuous and adequate monitoring are urgently necessary, as only quality results will enable us to prove the rationality of completed and planned shutdown works. After final shutdown of the mine, the monitoring results will reveal the quality of the closure activity. If observations and measurements do not point to any negative consequences of pit flooding up to the IX^{th} level, the pit will be flooded up to the IV^{th} level. The mine will be shut down by the end of the year 2006. However, the shutdown programme foresees the monitoring and observation of the consequences of mine closure for at least 3–5 years after the final shutdown of the mine.

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