CONSEQUENCES OF THE USE OF ORE RESIDUES FOR BACKFILLING OF PIT AREAS AND ITS INFLUENCE ON THE QUALITY OF MINE WATERS

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ABSTRACT

During the implementation of the Shutdown of the Idrija Mine projekt (Bajželj et al., 1996), which also includes the flooding of underground facilities, there appeared in 1995 the problem of increased concentrations of iron and sulphate ions and occasionally of waste oils in the pit water discharged into the Idrijca River from two interconnected pools on level XI.

Changes in the pumping regime and the conditions of pit water discharge into the river substantially reduced the contamination of the river – in particular the unpleasant colouring of riverbanks with the settled, orange-brown Fe-oxyhydroxides. Available data on the properties of materials used in the backfilling of pit areas during several hundred years of the mine's operation indicate that the sudden increased concentration of toxic components in pit water as the consequence of decomposition of deposited materials may be expected in future.

GEOLOGICAL CHARACTERISTICS OF THE IDRIJA ORE DEPOSIT AND TECHNOLOGICAL DEVELOPMENT OF Hg EXTRACTION

The Idrija ore deposit is of Middle Triassic origin and comprised of mineralized petrographic rocks (Carboniferous shale, sandstone, dolomites, conglomerate and partly also limestone), while the Upper Triassic rocks and Cretaceous limestones are not mineralized. Characteristic of the ore deposit is the nonuniform distribution of mercury ore appearing as cinnabar (HgS), and native mercury in rocks of varying properties and composition. The largest quantities of native Hg are found in Carboniferous shale, claystone and siltstone with intercalations of quartz sandstone. The mineralized clastic rocks contain on average 0.38% Hg. Approximately 50% of Hg appears is in the form of cinnabar, and the remainder as native mercury.

Over a period of 500 years, the ore processing technology changed constantly, from simple burning and smelting in iron and clay vessels with the addition of limestone, to burning in cast-iron retorts. In the last decades of operation of the pit and smelting plant, ore was burned in rotary furnaces.

Ore burning residues were deposited at various locations in Idrija and its surroundings, even in abandoned pit facilities. Today, burning residues represent a complex problem not only because of their constantly growing quantities resulting from increased production and lower Hg content in ore, but also because of technological development and modifications introduced in the ore burning process in various periods, as well as the subsequent treatment of ore burning residues (Čar, 1996).

Materials used for backfilling abandoned pit facilities

With the aim of reducing to the highest possible degree the influence of mining and smelting activities on the environment, part of the waste materials produced during the exploitation of Hg ore was deposited in abandoned pit facilities. As regards their properties, backfilling materials may be divided into four types:

1. in the initial phase, mine areas were backfilled with gangue produced during ore excavation. The technology available at the time did not allow for the profitable exploitation of mineral ore with low Hg content (0.5%). With the development of pyrometallurgical procedures, which enabled the processing of poorer ore, the backfilling material began to be repeatedly excavated in the seventies for processing in furnaces (mine faces Trije Kralji and Čemernik);

2. gangue minerals (dolomite, conglomerate) excavated for two purposes - the backfilling of pit facilities and access to new ore locations;

3. gangue minerals (dolomite) from quarries in the surroundings of Idrija;

4. ore residues from the smelting plant which, depending on ore enrichment, contain from 0.004 - 0.007% Hg in various forms (sulphides, sulphates and elemental mercury).

Investigations of abandoned, backfilled shafts have revealed that the material used for backfilling individual sections is not of a uniform type, but may be extremely heterogeneous. Furthermore, the quantitative structure of individual types of backfilling materials in different sections remains unknown.

Influences of the use of ore burning residues on the quality of mine water

Within the scope of the project involving the shutdown of the Idrija Mine (flooding of pit areas), sudden increases in the value of total iron (Fe_{TOT}) and sulphate ions (SO_4^{2-}) in the water collected in two interconnected pools on level XI. were detected (Figure 1). The Hg concentrations did not exceed the maximum admissible values.
Mine water and partly also atmospheric water is collected in two pools after penetrating through the ore deposit. The results of monitoring the chemical composition of water

samples (Table 1) over a period of 19 months (January 1995 - July 1996) led to the assumption that the increased concentrations of Fe_{TOT} and sulphate ions occurred primarily due to the leaching of products of decomposition of materials deposited in the mine in the past - burning wastes produced during pyrometallurgical extraction of ore rich in pyrite, and partly due to uncontrolled collapses in the flooded part of the pit (opening of larger areas and pyrite veins, confirmed by the water flowing from the Maver jack pit and the Inhaghi shaft on level XI).

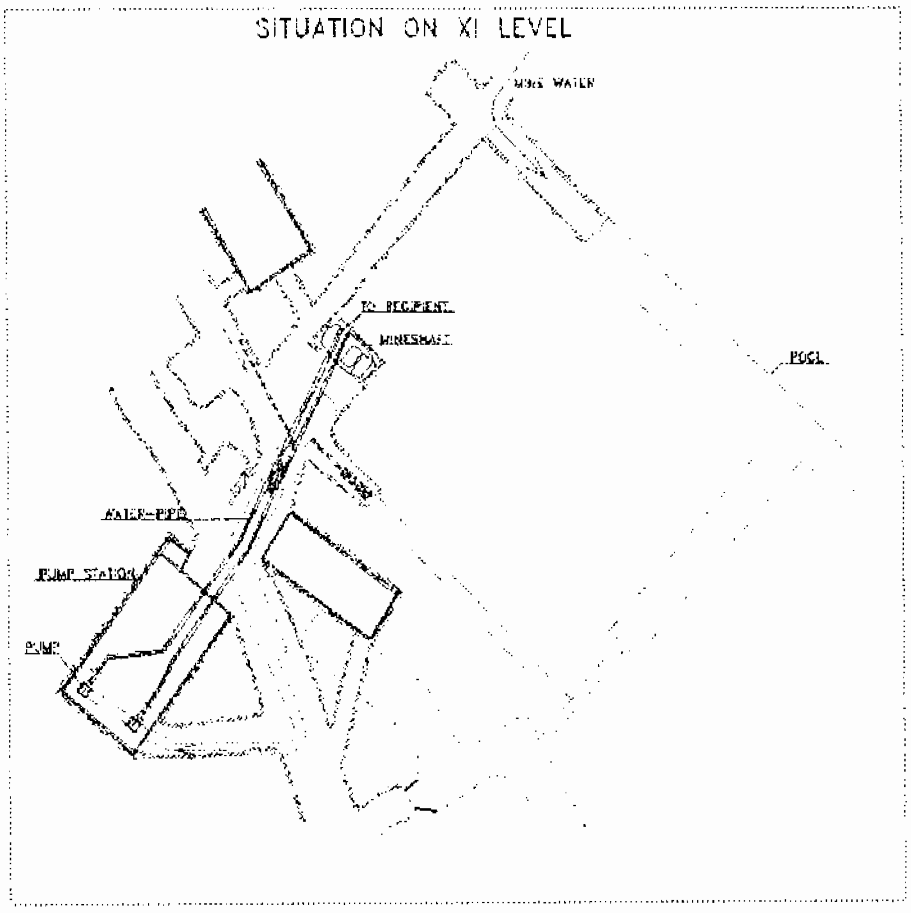

Figure 1: Schematic presentation of pools on level XI.

Table 1: Monitoring of chemical composition of pit water discharged into the Idrijca River in the period from 1995 - 1996

Date	**pH**	**$\mu S.cm^{-1}$**	**$Fe_{TOT}(mg.L^{-1})$**	**$SO_4^{2-}(mg.L^{-1})$**	**$Hg(ng.L^{-1})$**
1995					
09.01.*	7.8	460	0.02	64	4.8[1]
14.01.	7.5	9020	14.90	22	3.1[1]
16.02	7.5	6570	8.00	6240	6.7[1]
02.03.	8.1	5430	3.90	4100	8.0[1]
13.03.	7.8	7860	3.90	6500	26.0[1]
28.03.*	8.3	313	0.05	21	-
29.03.	7.5	5555	4.05	4813	-
30.03	7.9	3880	1.26	2875	-
30.03.	8.3	1102	0.09	345	-
03.04.*	8.5	314	0.03	16	2.0
04.04	8.3	2850	1.45	3750	-
11.04.	8.3	2850	1.45	3750	-
12.04.	7.9	7300	6.25	8250	-
13.04.	7.9	7610	4.75	6500	-
18.04.	7.9	6090	3.20	7250	-
03.05.	7.9	7450	5.30	8250	-
04.05.	7.8	7560	5.95	7750	-
21.05.	-	-	4.63	4750	-
12.06.	8.2	5830	3.81	5250	-
03.07.	8.4	3420	1.70	2500	-
21.09.	8.1	2080	2.63	1040	-
10.10.	7.8	6120	2.75	3060	-
21.11.	7.7	5610	2.13	2810	-
1996					
14.02.	7.7	4600	2.75	6437	-
16.04.	8.1	2820	1.04	2125	240[2]
29.05.	8.2	1907	0.66	1300	547[2]
30.07.	7.1	3520	1.35	2150	165[2]
31.07.	7.2	4610	1.80	3000	95[2]

- pupms were not operating

[1] reactive Hg

[2] total Hg

Chemical analysis of mine water

TPTZ and photometry (range 0 - 1.8 mg.L^{-1}) were used to determine the total iron content (Fe_{TOT}) in diluted pit water samples.

The quantitative presence of sulphate ions (SO_4^{2-}) was determined using the turbidimetric method, followed by photometric determination (range 0 - 70 mg.L^{-1}) in diluted pit water samples.

After UV oxidation, the total Hg content (Hg_{TOT}) in pit water was determined by means of cold vapour atomic absorption spectrophotometry (CVAAS). Initially, only reactive Hg was determined by the direct reduction of the water sample and CVAAS (DL = 0.5 mg.L^{-1}).

FINDINGS AND DISCUSSION

During the smelting of mercury ore in the presence of oxygen, cinnabar (850°C) reacts as follows:

$$HgS + O_2 \rightarrow Hg + SO_2 \qquad /1/$$

In the smelting of cinnabar ore rich in pyrite, Fe(II)-sulphate reacts with oxygen:

$$FeS + 2O_2 \rightarrow FeSO_4 \qquad /2/$$

Fe(II)-sulphate present in materials deposited in the pit most probably reacts with atmospheric water penetrating through the ore deposit and pit water to produce alkaline Fe(III)-sulphate:

$$FeSO_4 + H_2O + 1/2O_2 \rightarrow 2Fe\,(OH)SO_4 \qquad /3/$$

Due to the properties of water (pH ~ 7.8 - 8.0) in the mine area and the concentrations of iron ions, the transformation of iron into the insoluble hydroxide form $Fe(OH)_3$ (Fig. 2) is probable.

The chemical reactions and leaching of decomposition products of materials deposited into the pit in the past have led to the formation of red, iron-bearing slurry (Table 2) in abandoned pit areas, as well as to increased concentrations of Fe_{TOT} (up to 14 mg.L^{-1}) and sulphate ions (even up to several thousand mgL^{-1}) in the water collecting in pools on level XI, which is discharged twice daily into the Idrijca River (Table 1). The colouring of river banks in the beginning of 1995 by deposited orange-brown Fe-precipitate has not only spoiled the esthetic appearance of the river, but also endangered the fauna and flora of the biotope due to substantially exceeded MAC.

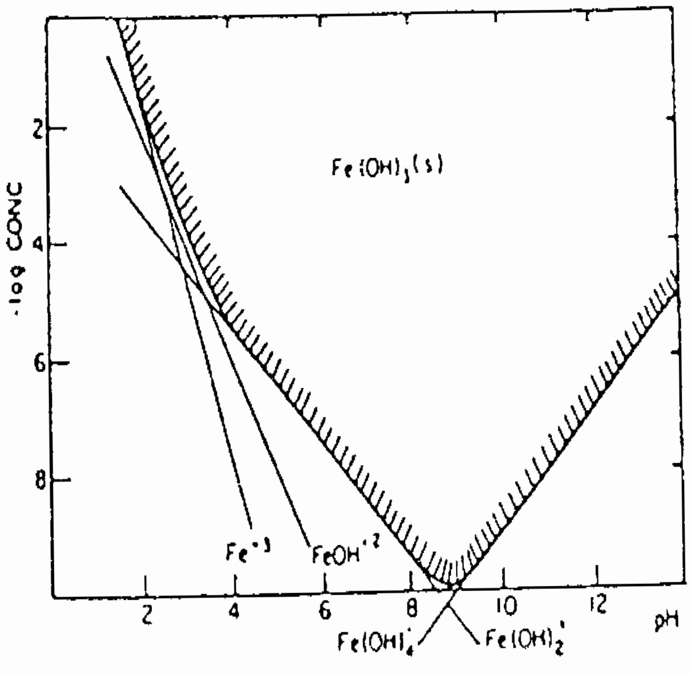

Figure 2: Solubility of amorphous FeOOH as a function of concentration and pH of medium[3]

Table 2: Composition of red iron-bearing slurry (analized 02.12.1996)

Parameter	Slurry	Water under the slurry
Fe (mg.g^{-1})	454	-
Hg (µg.g^{-1})	0.07	-
PH		7.13
Conductivity (µS.cm^{-1})		4320
Fe^{2+} (mg.L^{-1})		0
Fe^{3+} (mg.L^{-1})		0.04
Fe_{tot} (mg.L^{-1})		0.04
SO_4^{2-}(mg.L^{-1})		3437
Ca^{2+} (mg.L^{-1})		513
Mg^{2+}(mg.L^{-1})		539
Hg (µg.L^{-1})		0.014

Laboratory purification of mine water collected in the pools on Level XI

With the aim of purifying mine water, prior to its discharge into the outlet channel, to the level prescribed by Slovene laws, laboratory tests were carried out in 1995 at the Institute of Mining, Geotechnology and Environment using water samples taken during various time intervals of the pump's operation. In view of the varying concentrations of present iron (3 - 8 mg Fe.L^{-1}) and sulphates (5300 - 6500 mg SO_4^{2-} .L^{-1}), a series of precipitation, sedimentation, aeration and sorption tests were performed. The pH of water was regulated to the optimal value for the precipitation of iron present by the addition of a 1% solution of $Ca(OH)_2$ and the present sulphates were precipitated with the addition of 1% $BaCl_2$. After sedimentation, the liquid phase was led into the aeration zone and then into the outlet (Figure 3).

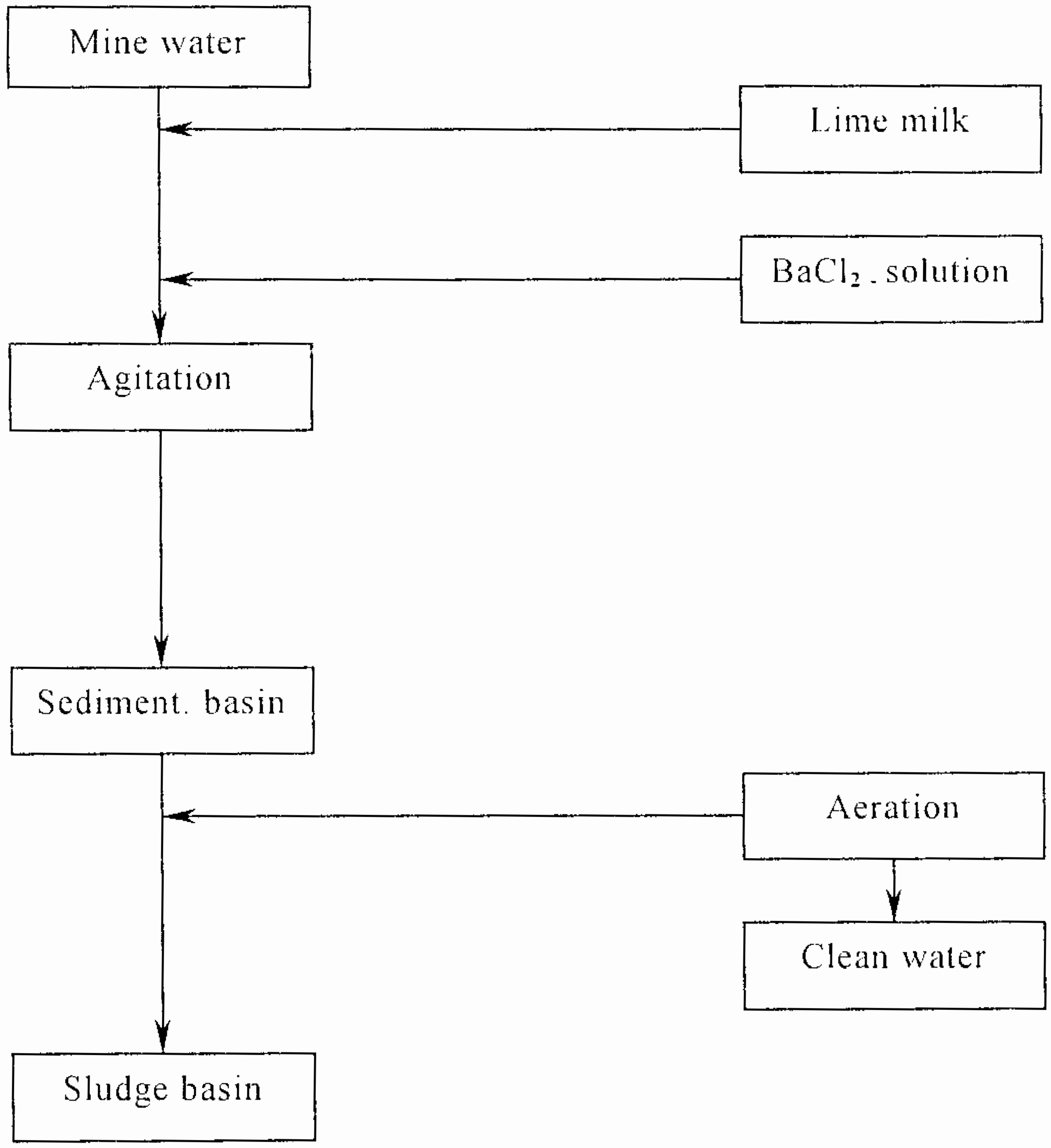

Figure 3: Schematic presentation of mine water purification

The results of chemical analyses (Table 3) have shown that the selected treatment is capable of reducing the iron content to traces and reducing sulphate concentrations by 60%. In view of the structure of pools and the locations of pumps, the addition of a limestone milk suspension into the pool was proposed. The liquid should then be directed into the aeration zone and later into the outlet channel. If the proposed procedure were introduced by the Idrija Mine, it would also be necessary to find a solution to the problem of depositing voluminous slurry. For this reason, the mine decided to make changes in the pumping regime and the conditions of pit water discharge into the Idrijca River.

Table 3: Results of laboratory purification of pit water from pools on level XI

Sample	**Parameters**					**Efficiency (%)**		
	PH	µS.cm^{-1}	Fe$_{tot}$ (mg.L^{-1})	SO$_4^{2-}$ (mg.L^{-1})	Hg (ng.L^{-1})	Fe$_{TOT}$	SO$_4^{2-}$	Hg
Feed I	7.9	6570	8.00	5300	25.6			
Sedimentation	8.8	4410	0.10	3300	10.0	98.7	37.7	60.9
Aeration	7.5	4500	0.01	2100	0.50	99.9	60.4	99.9
Feed II	7.5	6270	3.9	6500	26.0			
Sedimentation	8.7	6340	0.05	5500	5.0	98.7	15.4	80.7
Aeration	8.3	6230	0.01	6500	4.0	99.7	0.0	84.0

Further monitoring of pit water contamination performed in the second half of 1996 and in 1997 (Table 4) has confirmed our assumptions that the situation may be stabilized by natural processes - bringing iron concentrations below the maximum admissible values. Due to processes in the pit, the problem of increased concentrations of sulphate ions, which are occasionally extremely high (more than 600 mg.L^{-1}), but on average range from 1500 - 3000 mg.L^{-1}, has remained unaddressed to this day.

Table 4: Results of chemical analysis of pit water from pools on level XI in the period from 1996 - 1997

Date	**pH**	**µS.cm^{-1}**	**Fe$_{TOT}$ (mg.L^{-1})**	**SO$_4^{2-}$(mg.L^{-1})**	**Hg (ng.L^{-1})**
1996					
29.10.*	8.1	336	0.02	-	62
27.11.	8.2	4180	1.56	3375	266[1]
1977					
22.01.	7.9	4070	1.70	3375	981[1]
03.04.	7.9	4140	1.60	3500	132[1]

* pupms were not operating

[1] total Hg

By the introduction of changes in the pumping regime (reducing the risk of pumping Fe-precipitate settled on the bottom of pools) and in the conditions of discharging mine water into the Idrijca River, the contamination of the river - particularly the unpleasant colouring of river banks with orange-brown Fe-oxyhydroxides, has decreased.

In future phases of the flooding of pit areas, sudden increases in the concentrations of certain components of mine waters being discharged into the Idrijca River due to the leaching of products of backfill decomposition may be expected.

CONCLUSION

During the phase of closing down the mine and flooding the pit of the Idrija Mine, increased concentrations of Fe_{TOT} and sulphates (above MAC) in water being collected in two pools and then discharged twice daily into the Idrijca River were detected after flooding of the pit up to level XI. The Hg concentration did not exceed MAC.

Increased concentrations of Fe_{TOT} and sulphate ions were found to be the consequence of washing old backfills in mine sections where ore residues were used as backfilling materials. These ore residues were probably produced during the pyrometallurgical process of extracting Hg from ore rich in pyrite. In view of the fact that a variety of materials have been used for backfilling purposes in the mine's five hundred-year history, it is presently very difficult to foresee what will and may happen with these backfills during the flooding of pit areas. For this reason, continuous monitoring of the chemical composition of pit water at outfall is of utmost importance. However, despite these measures, unexpected occurrences cannot be excluded.

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