Górnictwo i Geoinżynieria • Rok 29 • Zeszyt 3/2 • 2005

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# TESTS OF PRECIPITATION OF SULPHATES FROM MINING WATER

The objective of these tests was to verify a methodology of desulphatation, which was developed at the Institute of Environmental Engineering, Faculty of Mining and Geology, Technical University Ostrava, separately for mining water with high concentration of sulphates and on the other hand for mining water with limited concentration of sulphates. The water samples used for these tests came from Smolník and Zlaté Hory.

## 1. Characterization of mining water from Smolnik location

In the eastern part of Slovakia, the water coming from a former mine of Smolnik has the biggest concentration of sulphates. The mine of Smolnik is one of the oldest ones in Europe.

The extraction in this mine was focused originally on copper ore. Gold, silver and iron were produced from this ore. Later a technology used for recovering copper from so-called cementation waters was developed. These waters developed naturally by oxidation and successive formation of the sulphates. The expansion of the mining industry towards extracting pyrite continued in the 20th century. The whole activity concentrated especially in the area of Pech pit. At the end of the eighties the mining activity was stopped and an implementation of a closure programme started. Since December 1990, flooding of the mine began. During this period, the quality of the water of the Smolnik stream improved, pH moved between 6–7 and metal content did not exceed the allowed limits. The flooding ended in the summer of 1994 and the quality of the surface water started to deteriorate rapidly. For the tests a sample of water flowing out of the Pech pit was used [1].

The pH of this water is 3.34 and sulphate concentration calculated as an average of three measured values is 2984 mg/l.

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## 2. Characterization of mining water from Zlaté Hory location

Underground mining of gold in the region of Zlaté Hory developed in the 13th century. A big expansion of the mining industry was between the years 1477−1603. Then a thirty-year long war started which resulted in a decline of this industry and the exhaustion of secondary raw materials of gold. The ultimate end of the mining activity is dated as the year 1883. A modern history of the ore-mining district in Zlaté Hory is dated by the year 1952, when a geological prospecting provided by surface bores, started. Among the first tested pockets were the ZH-west and ZH-east pockets. The prospecting continued with shaft sinking, crosscutting and driving of tunnels. A new pocket, ZH-south, was also discovered by surface boring. The prospecting also extended into the ZH-Mining Rocks pocket. Both these pockets are formed just out of the copper minerals. In 1965 construction of the RD Zlaté Hory plant was completed and in this year mining of the ZH-south pocket started. After the exhaustion of this pocket mining works moved to the ZH-Mining Rocks pocket. This pocket remained unexploited due to the low mineral content of the ore. The mining activity passed on to the complex ores (Cu, Zn, Pb, Ag) of the ZH-east pocket. Mining of Cu, Zn and Au from the ZH-west pocket followed speedily. The mining activity was stopped by the declaration of a closure programme for this pocket in 1993 [2].

TABLE 1

**Chemical composition of mining water from Zlaté Hory [3]**

| Year | Flow rate [l/s] | pH | SS [mg/] | DS [mg/l] | Cu [mg/l] | Pb [mg/] | Zn [mg/] | Mn [mg/l] | Fe [mg/l] | $SO_4^{2-}$ [mg/l] |
|---|---|---|---|---|---|---|---|---|---|---|
| 1990 | 78,1 | 11,9 | 536 | 503 | 2,6 | 0,12 | 3,16 | 5,5 | 25,2 | 206 |
| 1991 | 102,5 | 11,6 | 1396 | 894 | 11,75 | 2,08 | 13 | 7 | 59 | 407 |
| 1992 | 95,27 | 11,3 | 559 | 716 | 5,7 | 0,1 | 7,6 | 5.4 | 37,6 | 330 |
| 1993 | 79,18 | 11,5 | 1697 | 1328 | 6,5 | 0,02 | 10 | 8,5 | 57,9 | 306 |
| 1994 | 70,1 | 11,3 | 815 | 842 | 9,6 | 1,5 | 76 | 6 | 50 | 396 |
| 1995 | 64,32 | 3 | 79 | 692 | 7,58 | 0,1 | 17,65 | 5,7 | 38,6 | 422 |
| 1996 | 76,1 | 3,2 | 104 | 788 | 9,23 | 0,08 | 16,27 | 5,87 | 41,75 | 436 |
| 1997 | 64,8 | 3,2 | 71 | 659 | 9,55 | 0,04 | 14,12 | 5,48 | 49,54 | 389 |
| 1st half of 98 | 61 | 3,2 | 53 | 597 | 6,55 | 0,03 | 13,2 | 3,54 | 29,21 | 368 |
| 2nd half of 98 | 52,4 | 3,4 | 46 | 666 | 5,29 | 0,08 | 12,9 | 3,17 | 16,2 | 380 |
| 1999 | 69,5 | 3,8 | 38 | 680 | 4,64 | 0,01 | 12,33 | 2 | 11,25 | 432 |
| 2000 | 64 | 4,3 | 42 | 614 | 4,43 | 0,01 | 10,02 | 3,75 | 14,72 | 372 |

DS — dissolved solids
SS — suspended solids

An overview of the results of tests of the mining water flowing out of the adit to the surface during 1990−2000 (Tab. 1):

— 1st period, from 1994 inclusive — neutralization of the mining water by lime was done underground before the adit intake;

— 2nd period, from 1995 to the middle of 1998 — the mine water was cleaned by the current system of mine water treatment (neutralization at the adit collar);

— 3rd period, from the middle of 1998 — the underground area was flooded. Since then the mining water discharge out of the adit by gravity feed [3].

The character of mining water has not changed notably since 2000 until now.

## 3. Chemical precipitation of sulphates according to the methodology of the Institute of Environmental Engineering, Faculty of Mining and Geology, Technical University Ostrava

The aim of the particular stages of the research work concerning mine water desulphatation, was mainly to test the effect of the available coagulants. Based on the results obtained, the process of chemical precipitation using a combination of ions $Ca^{2+}$, $Al^{3+}$, $OH^{-}$, $AlO_2^{-}$, was chosen as a next method. The probable process of precipitation is as follows:

$$3SO_4^{2-} + 6Ca^{2+} + 2AlO_2^{-} + 4OH^{-} + 29H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O \qquad (1)$$

or

$$3Na_2SO_4 + 6Ca(OH)_2 + AlCl_3 + 26H_2O \rightarrow Ca_6Al_2[SO_4(OH)_4]_3 \cdot 26H_2O + 6NaCl \quad (2)$$

The final product of the above mentioned reactions (1), (2) is ettringit [4].

When the sulphates are chemically precipitating, the ettringite phase has the form of cryptocrystallic, light dispersive coagulation. This coagulation becomes crystallic after repeated drying and rehydratation [5].

Ettringit is generally expressed by the formula $Ca_6Al_2[SO_4(OH)_4]_3$, where the Ca::Al:$SO_4$ ratio is 6:2:3.

## 4. Desulphatation of mine water from Smolnik by sodium aluminate

The concentration of sulphate ions in the tested water, calculated as an average of three measured values was 2984 mg/l with pH 3.34.

The precipitation runs quantitatively at pH above 12.4. To achieve such a pH, it is necessary to add 5−5.6 g of $Ca(OH)_2$ to every litre of treated water.

To precipitate the ions of $SO_4^{2-}$, a reagent ALR-F was used. It is a concentrated solution of sodium aluminate, with a 17% active aluminium content.

### 4.1. Precipitation of $SO_4^{2-}$ ions in the presence of $Ca(OH)_2$, without ALR-F reagent

Methodology of the precipitation process (Tab. 2).

1. $Ca(OH)_2^{-}$ — 15 minutes of mixing at 200 r.p.m.
2. Filtration of the suspension.
3. Determination of sulphate concentration and pH value.

TABLE 2

**Desulphatation results 1**

| No. | $Ca(OH)_2$ [g/l] | pH | $SO_4^{2-}$ [mg/l] | Effect of desulphatation [%] |
|---|---|---|---|---|
| 1. | 6 | 12.59 | 2400 | 19.6 |
| 2. | 8 | 12.60 | 2362 | 20.8 |
| 3. | 10 | 12.61 | 2385 | 20.1 |

## 4.2. Precipitation of $SO_4^{2-}$ ions in the presence of $Ca(OH)_2$ and ALR-F reagent

Methodology of the precipitation process (Tab. 3).

1. $Ca(OH)_2^-$ — 15 minutes of mixing at 200 r.p.m.
2. ALR-F — 30 minutes of mixing at 200 r.p.m.
3. Filtration of the suspension.
4. Determination of sulphate concentration and pH value.

TABLE 3

**Desulphatation results 2**

| No. | $Ca(OH)_2$ [g/l] | ALR-F [ml/l] | pH | $SO_4^{2-}$ [mg/l] | Effect of desulphatation [%] |
|---|---|---|---|---|---|
| 1. | 4.0 | 2.0 | 12.21 | 598.4 | 79.9 |
| 2. | 4.0 | 4.0 | 12.38 | 570 | 80.1 |
| 3. | 4.0 | 3.0 | 12.28 | 444.8 | 85.1 |
| 4. | 4.6 | 3.0 | 12.49 | 220.6 | 92.6 |
| 5. | 5.2 | 3.0 | 12.55 | 495.8 | 83.4 |
| 6. | 5.5 | 3.0 | 12.58 | 188.0 | 96.1 |

TABLE 4

**Desulphatation results 3**

| No. | $Ca(OH)_2$ [g/l] | ALR-F [ml/l] | pH | $SO_4^{2-}$ [mg/l] | Effect of desulphatation [%] |
|---|---|---|---|---|---|
| 1. | 5.4 | 2.4 | 12.58 | 479.0 | 83.9 |
| 2. | 5.4 | 3.0 | 12.58 | 132.9 | 95.5 |
| 3. | 5.4 | 3.4 | 12.58 | 80.5 | 97.3 |
| 4. | 5.4 | 4.0 | 12.58 | 116.6 | 96.0 |
| 5. | 5.6 | 2.4 | 12.59 | 238.0 | 92.0 |
| 6. | 5.6 | 3.0 | 12.59 | 26.8 | 99.1 |
| 7. | 5.6 | 4.0 | 12.56 | 91.5 | 96.9 |
| 8. | 5.2 | 3.0 | 12.56 | 261.5 | 91.2 |
| 9. | 5.2 | 3.4 | 12.56 | 99.96 | 96.6 |
| 10. | 5.2 | 4.0 | 12.56 | 107.76 | 96.4 |

Based on the obtained results, we tried to find the optimum quantity of coagulants in following tests. The optimum quantity is the amount of coagulants, which will precipitate the sulphates to the lowest concentration. The results of this test can be found in Tables 4 and 5.

TABLE 5

**Desulphatation results 4**

| No. | $Ca(OH)_2$ [g/l] | ALR-F [ml/l] | pH | $SO_4^{2-}$ [mg/l] | Effect of desulphatation [%] |
|---|---|---|---|---|---|
| 1. | 5.2 | 3.2 | 12.56 | 118.28 | 96.03 |
| 2. | 5.2 | 3.4 | 12.56 | 199.6 | 93.31 |
| 3. | 5.2 | 3.6 | 12.56 | 49.92 | 98.32 |
| 4. | 5.2 | 3.8 | 12.56 | 45.28 | 98.48 |
| 5. | 5.4 | 3.2 | 12.56 | 64.4 | 97.84 |
| 6. | 5.4 | 3.4 | 12.56 | 123.28 | 95.87 |
| 7. | 5.4 | 3.6 | 12.55 | 65.0 | 97.82 |
| 8. | 5.4 | 3.8 | 12.55 | 49.64 | 98.33 |
| 9. | 5.6 | 3.2 | 12.58 | 114.4 | 96.17 |
| 10. | 5.6 | 3.4 | 12.58 | 42.96 | 98.56 |
| 11. | 5.6 | 3.6 | 12.58 | 0.48 | 99.98 |
| 12. | 5.6 | 3.8 | 12.58 | 0.97 | 99.97 |

## 5. Desulphatation of mine water from Zlaté Hory by sodium aluminate

Mine waters from the Zlate Hory location are different to the waters from Smolnik treated in the neutralization plant. Powdered lime is dosed so that the pH rises from 3–4 to the value of 8.5–9.5. The concentration of $SO_4^{2-}$ ions after the neutralization is 284.4 mg/l.

The concentration of the sulphates in the tested raw water, achieved as an average of three measured values was 343.8 mg/l with pH 3.39.

Coagulation proceeds quantitatively at pH above 12.4. To achieve such a pH, it is necessary to add 4 g $Ca(OH)_2$ to every litre of treated water.

### 5.1. Precipitation of $SO_4^{2-}$ ions in the presence of $Ca(OH)_2$, without ALR-F reagent

Methodology of the process of precipitation (Tab. 6).

1. $Ca(OH)_2$ — 15 minutes of mixing at 200 r.p.m.
2. Filtration of the suspension.
3. Determination of sulphate concentration and pH value.

TABLE 6

**Desulphatation results 5**

| No. | $Ca(OH)_2$ [g/l] | pH | $SO_4^{2-}$ [mg/l] | Effect of desulphatation [%] |
|---|---|---|---|---|
| 1. | 4 | 12.39 | 289.6 | 15.76 |
| 2. | 5 | 12.56 | 294.2 | 14.43 |
| 3. | 6 | 12.69 | 284.6 | 17.22 |

### 5.2. Precipitation of $SO_4^{2-}$ ions in the presence of $Ca(OH)_2$ and ALR-F reagent

Methodology of the process of precipitation (Tab. 7).

1. $Ca(OH)_2$ — 15 minutes of mixing at 200 r.p.m.
2. ALR-F — 30 minutes of mixing at 200 r.p.m.
3. Filtration of the suspension.
4. Determination of sulphate concentration and pH value.

TABLE 7

**Desulphatation results 6**

| No. | $Ca(OH)_2$ [g/l] | ALR-F [ml/l] | pH | $SO_4^{2-}$ [mg/l] | Effect of desulphatation [%] |
|---|---|---|---|---|---|
| 1. | 3 | 1.4 | 12.51 | 73.10 | 78.74 |
| 2. | 3 | 1.6 | 12.52 | 48.3 | 85.95 |
| 3. | 3.2 | 1.8 | 12.52 | 11.89 | 96.54 |
| 4. | 3.2 | 2.0 | 12.53 | 1.78 | 99.48 |
| 5. | 3.2 | 2.2 | 12.53 | 3.11 | 99.09 |
| 6. | 3.6 | 2.4 | 12.53 | 2.08 | 99.39 |
| 7. | 4 | 2 | 12.53 | 2.14 | 99.38 |
| 8. | 4 | 2.6 | 12.54 | 1.72 | 99.50 |
| 9. | 4 | 3.0 | 12.54 | 0.69 | 99.80 |
| 10. | 4.8 | 2.8 | 12.54 | 0.99 | 99.71 |

## 6. Conclusion

The goal of these tests was to prove the high efficiency of the methodology of desulphatation while removing $SO_4^{2-}$ ions and also to achieve the lowest possible concentration of sulphates in treated water when using this method. From the results quoted above emerges a conclusion that as for water with high concentration of sulphates (mining water from the Smolnik location), and also water with a practically null concentration, sulphates were removed with almost 100% effect.

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