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Environmental issues during clearing quarry waters Madneuli Mining Concentration Enterprise

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Abstract

The use of the elaborated technology enables to use low-graded barite ore by processing of which is acquired the independent product blanfix and sodium sulfide used as a reagent of non-solvent for deep purification of the acid quarry waters from ions of heavy metals with obtaining sulfide copper containing compounds fully useful for subsequent application.

1. **Introduction**

The permanent increase of production powers and intensification of getting minerals with speeding-up, redouble the degradation of quality of surroundings [1-3].

The formation of quarry waters, at the stripping and processing of deposits, which are soiled with ions of heavy metals, is one of the factors of destructive influence on nature. The stripping of deposits of copper and polymetal ores is the reason of soiling quarry waters with ions of copper, zinc, lead cadmium, chromium and etc. The quantity and composition of soiling elements depend on the tape and character of mines and also on climatic conditions. So the solution of ecological problems needs individual approach for each concrete deposit.

The wide geography of deposits of copper and polymetal ores (e. g. Stiluoter in USA, Sadbery in Canada, Chukikamata in Chile, Central African copper-bearing zone, Rio-Tinto in Spain, Kuroko in Japan and etc.) makes global character of this problem. It is naturally that any new technological decision or process, which is connected with the research of this problem for concrete deposit, will have an interest for others.

Madneuli Mining Concentration Enterprise (MMCE) is faced with the crucial problem of soiling of surroundings with ions of heavy metals. MMCE is one of the biggest. The main objective of the proposed work is enterprise in the region. It situated 90 km on the south-west of Tbilisi. Distinguishing feature of MMCE is that its products have a great demand on the World Market because of actual absence of arsenic in copper concentrate [4].

The main objective of the proposed work is purification of acid quarry waters (AQW), farming as a result of processing and exploitation of quarry of Madneuli mining plant (MMCE).The quarry waters are formed by atmospheric precipitation and subsoil waters at the stripping and processing of deposit of Madneuli barite complex ore. The ionic exchange happens as a result of contact of quarry waters with the rocks. The existence of pyrite and chalcopyrite in the rocks and the influence of air oxygen and carbothionic bacteria under the definite conditions are the reasons of the formation of acid quarry waters (AQW).

Content and discharge of AQW are within the wide limits and depend on climatic conditions and seasons. According to their content AQW belong under the salty waters of sulphate class. The annual average discharge of AQW makes 1, 000 000 m^3 [5].

The average content of the main ions in AQW (mg/l): Cu – 450-1200; Zn - 250-1100; Fe -500-1000; Pb – 0.20-0.70; Ni – 0.40-0.95; Co – 0.5-1.2; Cd – 0.9-2.85; pH AQW – 2.5-2.6.

In terms of content of contaminating substances (total quantity 2-5 g/l), these are waters of middle concentration, and in terns of aggressiveness – aggressive solutions.

The AQW physical-chemical indicators evidence a wide variation in composition of these waters, which requires a thorough selection of optimal treatment method.

The complex and changing composition of AQW-s, which is characterized by large volumes, extremely complicates use of wide-spread methods such as: membrane technology, use of ionites, electrochemical methods. So, the reagent method was chosen for AQW treatment as the most cheap and effective [5].

The most accessible and widespread reagents are burnt lime, burnt lime used as coagulant, sediment and chemical reagent, and also chlorinated lime, hypochlorite calcium and natrium, also sulphides and oxides of alkali and alkaline-earth metals.

2. The existing technology of AWQ treatment applied by the MCE envisages use of lime as depositing reagent and includes the following treatment stages: AQW pumping, locating under spoil bank, settling in settler (capacity – 5,000 m^3), cementation with active iron powder, filtration, neutralization by quicklime and dumping of residue (deposit) into tailing dump (Fig.1). Neutralized and clarified water is used for MCE-s needs. A shortcoming of such treatment is formation of a large quantity of slime which is hard to dehydrate and impossible to separate. Thus, its industrial use is complicated and does not take place. The water treatment scheme uses reagents (activated iron powder etc.) which are not manufactured in the country and their delivery creates additional technical problems. Cleared water contains a large quantity of calcium salts and it's hard to use it in circulating water supply.

Treatment of AQW-s with alkali reagents allows to reduce the metal content down to the figure comparable to the maximum concentration limit. Additionally, at the localization stage, AQW-s partially leak into the Mashavera River from tailing dump. Use of such waters for irrigation and household needs resulted in soil contamination with heavy metal ions. Thus, it's obvious that acid quarry waters of the Mining Concentration Enterprise need more thorough treatment without which no AQW discharge into nearby reservoirs should be allowed.

More thorough treatment can be achieved through AQW treatment with sulfides (Na_2S, H_2S, BaS). The explanation is that solubility of sulfides of heavy metals is significantly less than that of any other not readily soluble compounds (hydroxides, carbonates).

3. The proposed AQW treatment technology (Fig. 2) envisages application of sodium sulfide as depositing reagent (Na_2S) which is obtained through processing of stock in barite spoil banks. The quantity of these stocks is 1.8-2 million tons and their processing will ensure complete clearing of AQW-s during the entire operation of the MCE.

The proposed technological scheme of AQW clearing based on barite ore processing (Fig. 3) includes the following main stages:

I – barite reduction;

II – wet milling and leaching of reduced mass (fusion cake);

III – obtaining of blanfixe and depositing reagent;

IV – AQW treatment with the obtained sodium sulfide solution.

At stage II of the said scheme, by-product, sodium sulfide, obtained as a result of exchange reaction, serves as depositing reagent. At pH 4.0 –5.0, it ensures actually complete deposition of heavy metal ions according to the reaction:

$$Me^{2+} + S^{2-} \rightarrow MeS$$

The preliminary data (experiments with model solution) evidences that the said exchange reaction goes according to the laws of stoichiometry and the process kinetics is described by the exchange reaction.

pH values 4.5-5.0 are achieved by adding sodium sulfide, which serves both as depositing reagent and pH regulator. Heavy metal ions which are present in solutions are deposited as sulfides, with quite significant zinc deposition being achieved at pH 1.5, nickel and cobalt – at pH 3.3m copper, iron and cadmium – at pH 4.0-4.3. The said pH values are achieved due to sodium sulfide depositing reagent, with its own pH 11-12.

The conducted laboratory experiments showed that deposition of heavy metals lasts within 15-20 minutes and the AQW clearing achieves the values which are much lower than the maximum allowed concentration limits.

The laboratory research results on clearing acid quarry waters (AQW) of the Madneuli Mining Concentration Enterprise (MMCE) of heavy metal ions were checked using an assembled large laboratory-scale plant of a capacity of 10 liters, including precipitating reactor made of quartz glass, pH-meter, compressor (Fig. 3).

When comparing the treatment schemes (Figs. 1 and 2), it's easy to notice their significant differences. The depositing reagent used in the existing scheme-lime, is used for AQW clearing and neutralization. The obtained deposit, a mixture of hydroxides with calcium sulfite, cannot be separated, so it is not industrially used.

The proposed clearing scheme (Fig. 2) is more simple than the existing one (no stage of AQW clarification in tailing dump). The depositing reagent (Na_2S) used in this scheme allows, besides fine cleaning, to obtain heavy metals as sulfides which are easy to separate and thus ensures additional quantity of finished commercial product.

Fig. 4 shows the general technological scheme of barite ore processing and AQW clearing, which include obtaining the depositing reagent (Na_2S) and valuable commercial product, blanfixe ($BaSO_4$), is mostly based on local stock of the MCE [6, 7].

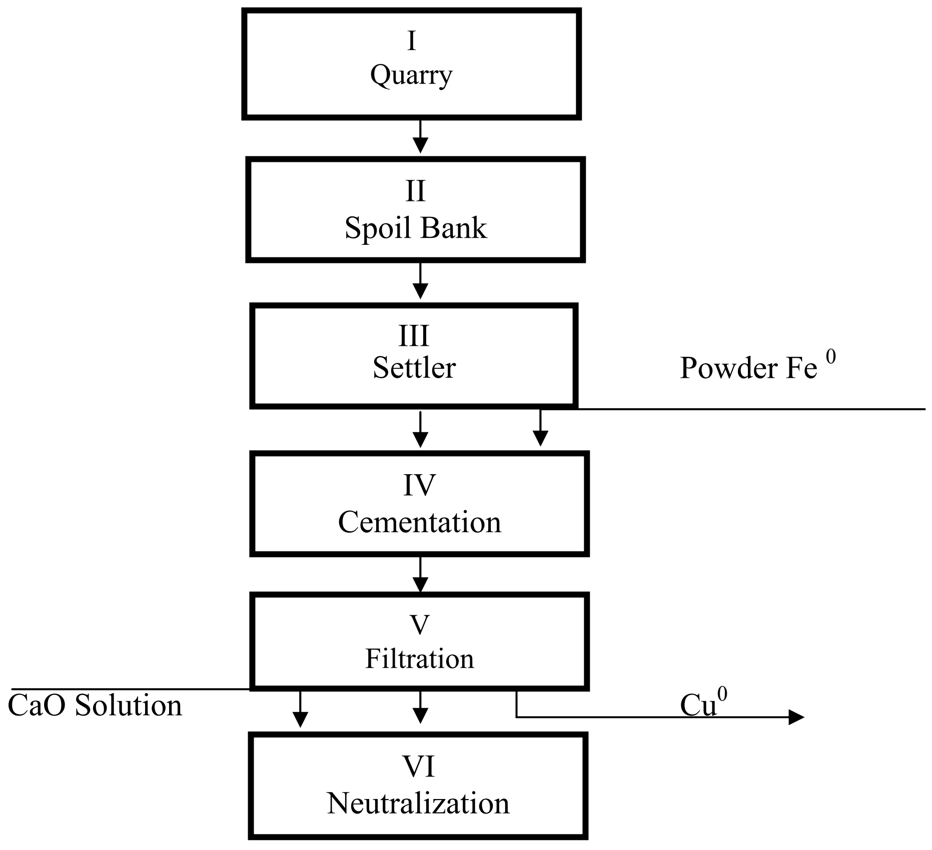
As heavy metals precipitate as sulfides (MCE'-s commercial product, copper concentrate, also contains the said metals in the form of sulfides), implementation of the proposed technology will allow the MCE to have 4-9 % more copper concentrate per year.

Noteworthy is that, besides AQW clearing, the proposed technology envisages use of barite in spoil banks, with obtaining an expensive commercial product – blanfixe ($BaSO_4$).

Cleared AQW will be mostly used as service water in the MCE water circulation system.

The expected economic effect from the realization of this technology without taking in consideration ecological effects approximately makes 0.8-1.2 million USD in a year.

Scheme 1



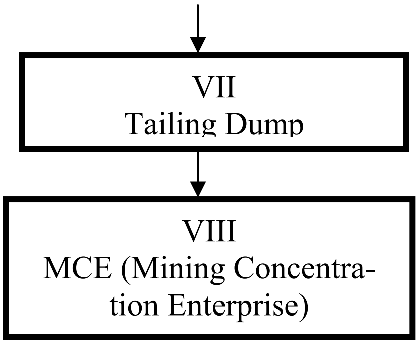


Fig. 1. The technological AQW treatment scheme applied by the MCE

The key shortcomings of the existing technology are:

- insufficient clearing of AQW-s;
- large consumption of additional reagents (quicklime, active iron powder);
- clogging the water circulation system with poorly soluble calcium compounds

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Scheme 2

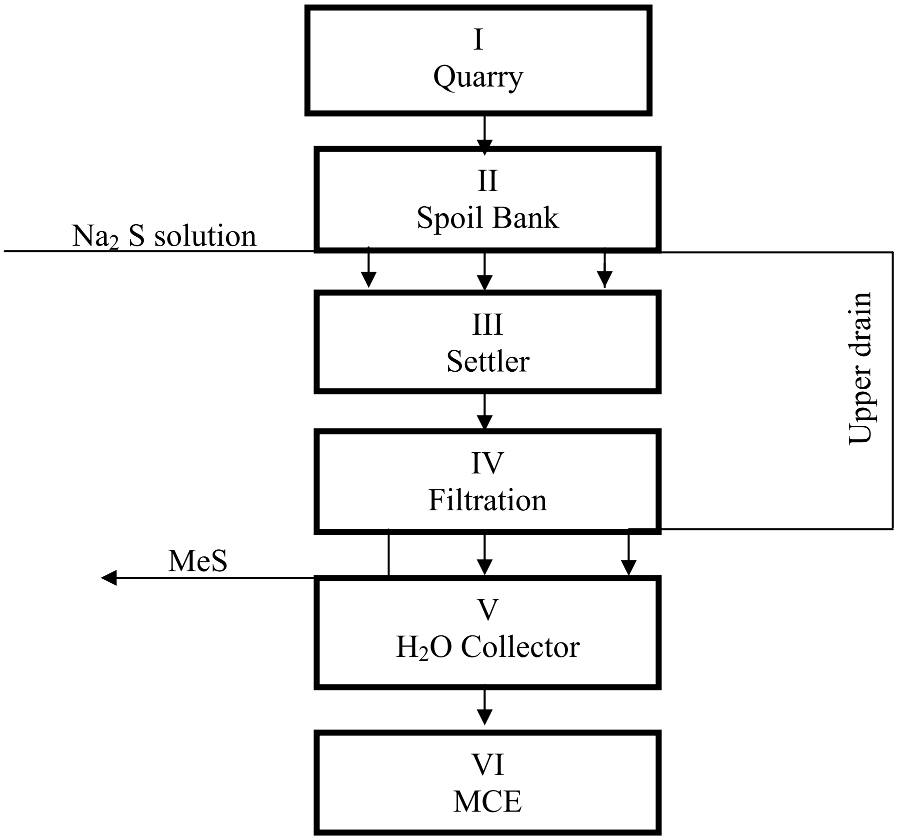

Fig. 2. Proposed technological AQW treatment scheme

The key advantages of the proposed technology are:

- fine AQW cleaning;
- utilization of valuable components;
- rational use of water resources.

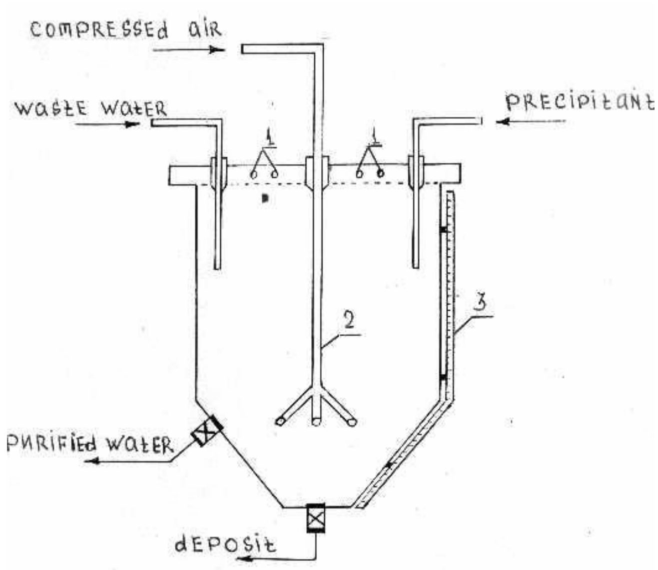

Fig. 3. Precipitator.
1. Holes for air duct ; 2. Bubbler 3. Meter.

Scheme 3

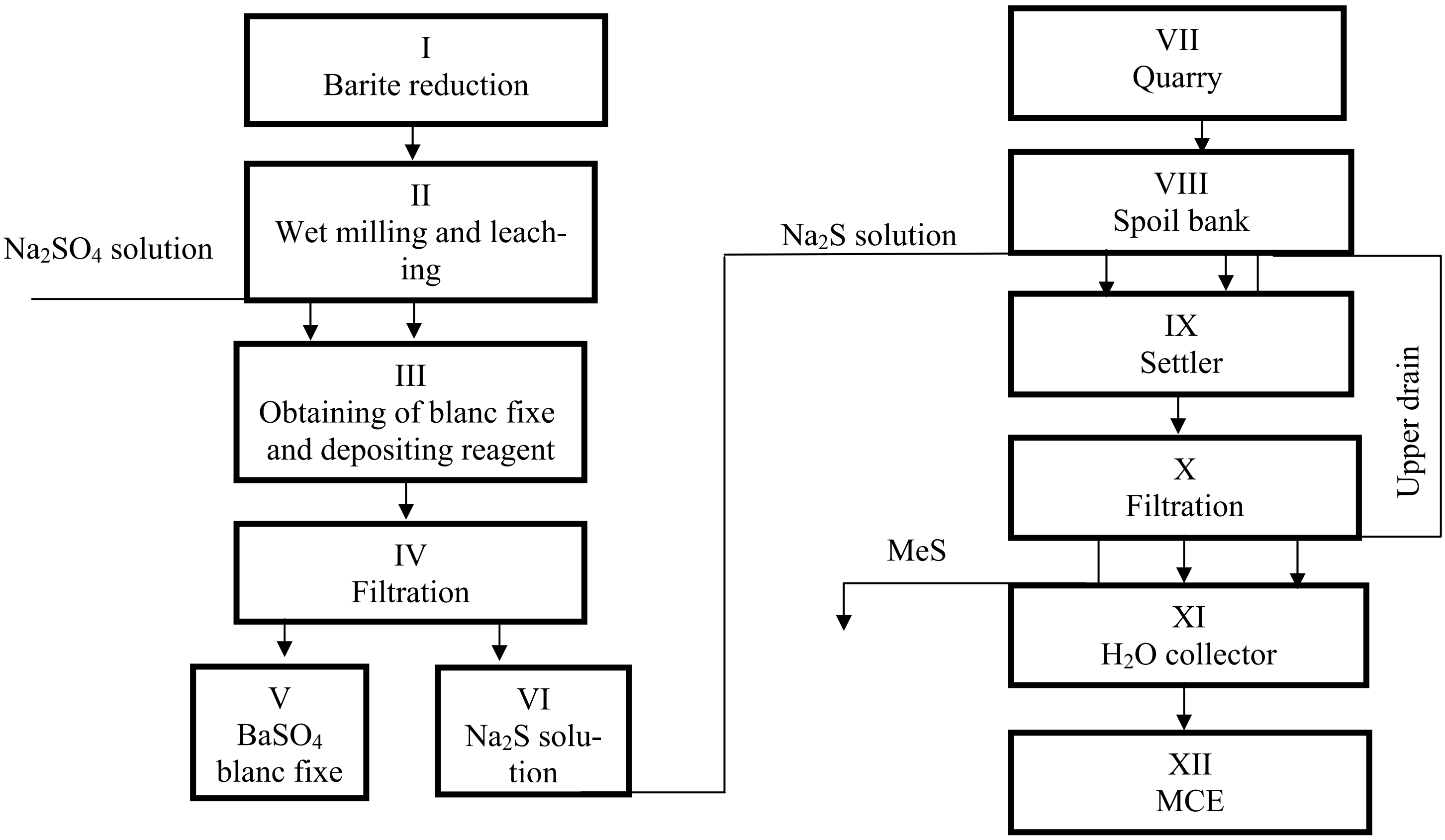

Fig. 4. General technological barite ore complex processing and AQW treatment system.

The key advantages of the proposed technology:

- use of barite stocks;

- obtaining depositing reagent (Na_2S);
- obtaining valuable blanfixe commercial product ($BaSO_4$)
- AQW fine cleaning;
- utilization of valuable components (CuS, FeS, ZnS);
- rational use of water resources;
- environmental improvement in the region.

4. Conclusion

The technology of purification of quarry waters on the basis of reprocessing barite concentrate has been developed in the process of which sulfide compounds are obtained used as chemical reagents of sediments. The technological parameters of reprocessing float-barite and purification of quarry waters have been determined. It is established that during use of the sulfide compound as reagents the deep purification of acid quarry waters from ions of heavy metals with acceptance of copper containing sulfide sediments useful for subsequent use is achieved.

References

[1] Pilipenko A. G., Gornovski I. T. et al., Complex process of mine waters. Kiev, Technica, 1985.
[2] Borbat V. F. Hydrometallurgy. Moscow, 1986.
[3] Andguladze Sh. N., Gaprindashvili V., Vasiliev B. Precipitation of arsenic by iron powder from the waste water in the pyrite cinder hydroseparator system of sulphuric acid production. Bullet. Acad. Sci. Georgian SSR. 1997, v. 93, N1.
[4] Andguladze Sh. The new technology cleaning of sour carrier waters in Madneuli Miningenrich Centre. Chem. Technology. Moscow, 2003, N1, pp. 20-22.
[5] Andguladze Sh.,.Mchedlishvili G, Berejiani A. Analysis of metal ion precipitating conditions of Madneuli Ore Minig Enterprise acid open-cut mine water. Proceed. Georgian National Acad. Sci.. Chemical series, 2009, v. 35. N 3. pp.396-397.
[6] Andguladze Sh.N. A new technology of purification of acid qurry waters in Madneuli Mining Concentration Enterprise. J. Chem. Technology, Moscow, 2003, N1, pp. 20-22.
[7] Andguladze Sh,.Gaphrindashvili V, Tchankotadze A., Kvinikadze T., B. Manning. Use of secondary raw materials for purification of acid qurry waters of Madneuli Ore Mining and Processing Enterprise. Georgian Chem. J., 2009, v. 9, N 4, pp. 362-364.

Решение экологических вопросов при очистке карьерных вод Маднеульского горнообогатительного комбината

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Резюме

Применение разработанной технологии позволяет использовать низкосортную баритовую руду, переработкой которой получается самостоятельный продукт бланфикс и сульфид натрия, используемой в качестве реагента осадителя для глубокой очистки

кислых карьерных вод от ионов тяжелых металлов с получением сульфидных медьсодержащих соединений вполне пригодных для дальнейшего применения.

მადნეულის სამთოგამამდიდრებელი კომბინატის კარიერული წყლების გასუფთავების ეკოლოგიური საკითხების გადაჭრის შესახებ

შალვა ნ. ანდღულაძე, ვახტანგ ნ. გაფრინდაშვილი, ნიკოლოზ შ. ანდღულაძე

რეზიუმე

დამუშავებული ტექნოლოგია იძლევა დაბალხარისხიანი ბარიტული მადნის გამოყენების შესაძლებლობას, რომლის გადამუშავების შედეგად მიიღება დამოუკიდებელი კონკურენტუნარიანი პროდუქტი ბლანფიქსი და ნატრიუმის სულფიდი, რომელიც თავის მხრივ გამოიყენება მჟავა კარიერული წყლების ღრმა გაწმენდისათვის მძიმე მეტალების იონებისაგან. აღნიშნული ტექნოლოგია იძლევა საშუალებას სპილენძშემცველი სულფიდების მიღების და მათი შემდგომი გამოყენების.