

## ENVIRONMENTAL IMPACTS AT COAL WASTE DISPOSAL SITES - EFFICIENCY OF DESULFURIZATION TECHNOLOGIES

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### ABSTRACT

During beneficiation of coal at the coal mining area of Tula, Russia, huge volumes of coal wastes with considerable residual pyrite content are produced. These wastes that are usually disposed of without specific care in the environment are active sources of coal mine drainage generation which severely contaminates soils, surface- and groundwater and endangers the ecosystems of the area.

In the present paper a complete environmental characterization research is carried out in order to determine the characteristics of the wastes, establish their acid generation potential, the leachability and bio-availability of several hazardous constituents and predict the environmental impacts at the disposal sites. Based on this data as well as on process parameters and disposal practices, an evaluation of desulphurization technologies is carried out.

Experimental studies reveal that these wastes are considered as permanent sources of coal mine drainage generation and therefore cause extensive contamination at the disposal sites. In addition, due to several technological constraints of the desulphurization technologies and the characteristics of the wastes, the potential of in situ desulphurization is considered low. Desulphurization technologies present a higher potential only if applied in the framework of an integrated waste management scheme.

### INTRODUCTION

At Tula coal region, 200 km south of Moscow, Russia, coal beneficiation wastes with high S content have been piled on over 150 dumps or disposed of in tailing dams. One of the most serious environmental problems associated with the surface disposal of coal wastes is the oxidation of the

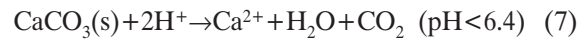
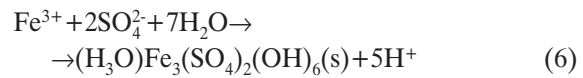
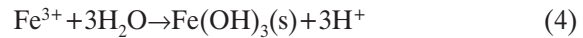
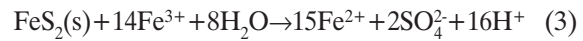
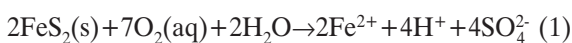
inherent pyrite and the generation of acidity. Oxidation of pyrite releases dissolved  $\text{Fe}^{+2}$ ,  $\text{SO}_4^{2-}$  and  $\text{H}^+$ , while the subsequent oxidation of  $\text{Fe}^{+2}$  to  $\text{Fe}^{+3}$  by chemical and/or biological means triggers further oxidation of the contained  $\text{FeS}_2$ . Coal mine drainage (CMD) is characterized by low pH

and varies widely in composition, with elevated concentration of sulphates, iron, manganese, aluminum, other toxic and radioactive ions as well as excessive total dissolved solids.

CMD from underground and surface mines, waste dumps and tailing dams is one of the oldest and most consistent industrial problem at coal mining regions of Russia and elsewhere. In most cases, it causes extensive contamination of shallow groundwater systems and soil water zones. Ferric iron, when discharged to surface water, hydrolyzes to produce hydrated iron oxides and additional acidity. The generated acidity lowers the pH of the water, making it thus corrosive and unable to support various forms of aquatic life. Impacts affect also agricultural activities, vegetation, industrial and potable water supplies, as well as the aquatic organism habitat. Toxicity levels depend mainly on discharge volume, pH, total acidity, concentration of dissolved metals and buffering capacity of the receiving streams. The buffering capacity is a function of the concentration of bicarbonate and carbonate ions.

The adverse environmental effects of CMD at the area under study are easily seen with on site observations. At the banks of tailing dams oxyhydroxides and iron sulphates, as a result of pyrite oxidation by chemical and biological means, are formed. In addition, due to soil acidification, most of the re-vegetation trials have failed; the remaining pine trees are in very poor condition with most of their needles being yellow. Furthermore, it has to be mentioned that in some parts of the broader Tula district, groundwater is not potable since elevated concentrations of toxic and radioactive elements have been detected. It is believed that mining activities have contributed, to some extent, to this contamination.

CMD is the result of the interactions of certain sulphide minerals with oxygen, water and bacteria. Iron sulphide minerals such as pyrite ( $\text{FeS}_2$ ), arsenopyrite ( $\text{FeAsS}$ ), chalcopyrite ( $\text{CuFeS}_2$ ) and others containing Fe, Cu, As, Sb, Bi, Se or Mo can produce acidic solutions upon oxidation. Pyrite is the major source of CMD generation in coal waste disposal sites. The main primary and secondary reactions involved in CMD production in such systems are shown in the following equations (1)-(8).



Reactions 1 and 2, describing the oxidation of sulfur and iron by  $\text{O}_2$  can be assisted by various species of sulfur and iron-oxidizing bacteria, such as *Thiobacillus Ferrooxidans*. Reaction 3 describes the oxidation of pyrite by dissolved ferric iron produced by reaction 2; at acidic pH, rates of pyrite oxidation by  $\text{Fe}^{3+}$  are much faster compared to oxidation by  $\text{O}_2$ . Part or all of  $\text{Fe}^{3+}$  may precipitate as  $\text{Fe}(\text{OH})_3$  or related compounds such as ferric sulfates or ferric oxyhydroxides, as seen in equations 4-6. Reactions 7 and 8 describe the dissolution of calcium carbonates and the formation of gypsum.

Mitigation of impacts caused by CMD can be effected by disposal of coal wastes in engineered tailing dams, comprising impermeable bottom and leachate collection systems. If no such practice is followed then remedial action is required. Remediation techniques aim either at minimization of precipitation infiltration within the waste mass or modification of their acid generation potential. Minimization of precipitation infiltration can be effected by isolation of the waste dumps from the environment with the application of composite/vegetative/wet covers, while modification of their acid generation potential can be effected by the addition of neutralizing/stabilizing agents (Komnitsas *et al.*, 1998; Hallett *et al.*, 1999). If waste characteristics are favorable, reduction of the pyrite content may be attempted by the use of physical, chemical, thermal or biological techniques. The advantage of desulphurization is the production of waste volumes with low sulphur content and therefore limited CMD generation potential. This volume with no or minimum treatment can be safely disposed of at the surface or used as backfill.

In the present paper a complete environmental characterization research is carried out in order to

determine the characteristics of the wastes, establish their acid generation potential, the leachability and bio-availability of several hazardous constituents and predict the environmental impacts at the disposal sites. Based on this data as well as on process parameters and disposal practices an evaluation of desulphurization technologies is carried out.

## MATERIALS AND METHODOLOGY

### Materials

Two representative samples of coal wastes, A and B, were collected from Kimovskiy tailings dam, 75 km east of Tula town, Russia. At this 7,000 ha coal mining area, several open pits operate since 1954. Kimovskiy wastes exhibit considerable diversity in composition regarding sulfur and metals content and vary in texture, containing coarse and fine particles; the particle size distribution depends mainly on the coal beneficiation treatment applied.

Both samples were initially oven dried at 60°C for 24 h to remove moisture and then sub-samples were crushed down to minus 2 mm and pulverized in order to perform the required analyses.

### Methodology

A detailed environmental characterization of the wastes was carried out by applying the following standard analytical techniques and leaching tests.

- Chemical analysis of the bulk samples; by digestion and measurement of the ion concentration in solution by Atomic Absorption Spectrophotometry (A.A.S); a graphite furnace was attached for analyses of trace elements. Loss of ignition was measured by heating the samples at 1000°C for 1 h. Total sulfur and carbon content was determined by a LECO analyzer. Forms of sulphur were determined according to the Russian equivalent to ASTM standard with a designation of D2492-90, re-approved in 1998.
- Mineralogical analysis; by X-ray diffraction (XRD, Siemens D5000 Diffractometer) using Cu-K $\alpha$  radiation.
- Particle size analysis; by wet screening.
- Acid Base Accounting (ABA) was employed to determine the Neutralisation Potential (NP) and Maximum Potential Acidity (MPA) of the wastes, expressed in kg CaCO<sub>3</sub> t<sup>-1</sup> of waste (Sobek *et al.*, 1978).

- Paste pH was determined at water to solid ratios equal to 2.
- The long-term stability of the wastes to acid leaching was determined with the U.S.EPA's Multiple Extraction Procedure (MEP), Method 1320 (US EPA, 1986). The wastes were subjected to leaching according to the Extraction Procedure Toxicity Test protocol and then the solids were re-extracted with a synthetic solution simulating acid rain conditions (H<sub>2</sub>SO<sub>4</sub>:HNO<sub>3</sub>, 60:40 w%, pH 3±0.2).
- The speciation of the toxic elements contained in the wastes in soluble or readily available form (exchangeable or carbonate fractions) was determined with the application of the first two stages of the Sequential Extraction Procedure (Tessier *et al.*, 1979). These stages involve leaching of the wastes with MgCl<sub>2</sub> (1<sup>st</sup> stage) and CH<sub>3</sub>COONa (2<sup>nd</sup> stage).
- The toxicity of the wastes was determined according to the Toxicity Characteristic Leaching Procedure (U.S. EPA TCLP, 1990).
- Isolation, identification and enumeration of soil microorganisms was carried out by standard methods (Groudeva *et al.*, 1993).
- The specific activity of the radionuclides was determined by an ORTEC spectrometer with a HPGe detector. The total effective specific activity (in Bq kg<sup>-1</sup>) was determined with the equation  $A_{\text{eff}} = A_{\text{Ra}} + 1.31A_{\text{Th}} + 0.085A_{\text{K}}$ .

Desulphurization tests under ambient temperature conditions were conducted in stirred laboratory reactors with temperature control under the following conditions: temperature: 30, 60 and 80°C, pulp density: 10% w v<sup>-1</sup>, time: 15, 60 and 120 min and KOH and HNO<sub>3</sub> concentration: 1 and 3 N.

## WASTE CHARACTERISTICS

The chemical analysis of the wastes, regarding major and trace elements, is presented in Table 1. According to this data, it is seen that the wastes are characterized by elevated concentration of S, C, Fe and Al. Average values regarding these elements are 13.5%, 10.6%, 10.7% and 3.2% respectively, indicating the presence of residual pyrite and carbon. Pyrite, due to oxidation and aluminium, due to hydrolysis, are major contributors to coal mine drainage. S is mainly present in the sulphide form (60-70%), but also sulphate S (30%) and organic S (10%) are detected. Sulphate S,

Table 1. Chemical analysis of coal wastes

Major Elements	A % w/w	B % w/w	Trace Elements	A mg kg <sup>-1</sup>	B mg kg <sup>-1</sup>
S, total	16.11	11.10	Pb	42	18
C, total	8.76	12.34	Zn	93	77
Fe(tot)	12.90	8.55	Cu	23	20
Si	16.12	21.11	Cd	3	1
Al	2.88	3.42	Mn	365	245
Ca	0.19	0.79	Cr	26	31
Mg	0.14	0.18	Ni	33	40
Ti	0.21	0.23	As	34	32
K	0.12	0.11	Sb	75	69
Na	0.14	0.13	Se	3	4

mainly present in surface samples, indicates oxidation of pyrite by direct and indirect mechanisms.

The concentration of trace elements, such as Mn, Sb, Zn, As, Pb and Cr is considered limited, but special attention should be paid if some of these ions are present in CMD due to their high toxicity.

Loss of ignition varies between 31 and 38% (for A and B respectively), while moisture content is approximately 7% for both samples.

A typical particle size analysis of the as received wastes is (%): +10 mm: 12.6, -10+2.5 mm: 21.6, -2.5+1.7 mm: 4.2, -1.7+1 mm: 7.6, -1+0.5 mm: 9.6, -0.5+0.125 mm: 14, 0.125+0.106 mm: 12.6, -0.106+0.053 mm: 9.2, -0.053 mm: 8.6, indicating a quite normal size distribution. According to this analysis the wastes can be characterized as fairly fine, since the -1 mm fraction accounts for over 50% of the total weight.

The specific effective activity of natural radionuclides is in general low and varies between 70 Bq kg<sup>-1</sup> for Th-232, 60 Bq kg<sup>-1</sup> for Ra-226 and 700 Bq kg<sup>-1</sup> for K-40. The total average effective specific activity is 210 Bq kg<sup>-1</sup>. This value is below the limit of 370 Bq kg<sup>-1</sup>, set in Russia for construction materials.

The main minerals identified by XRD are quartz, pyrite, carbon, kaolinite, illite, gypsum and jarosite-group minerals. Jarosites are hydroxyl iron sulphate compounds precipitating in acidic solutions. The content of acid consuming minerals is extremely low, indicating thus an extremely

limited neutralization potential of the coal wastes. The oxidation of pyrite is assisted by the presence of sulphur oxidizing bacteria. Acidophilic chemolithotrophic bacteria are the prevalent microorganisms in numbers exceeding 10<sup>7</sup> cells ml<sup>-1</sup>. *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* are the main species in this microbial community. Strains isolated from acidic waters reveal that these bacteria are able to oxidize Fe<sup>2+</sup>, S<sup>0</sup> and sulphide minerals such as pyrite, arsenopyrite and chalcopyrite. Some moderately thermophilic chemolithotrophic bacteria related to the genera *Thiobacillus* and *Sulfobacillus* were also isolated. Some acidophilic heterotrophic bacteria (mainly related to the genus *Acidiphilium*) were found but in low numbers (10<sup>2</sup>-10<sup>3</sup> cells ml<sup>-1</sup>). These bacteria use as sources of carbon and energy organic compounds secreted by the chemolithotrophs. Some neutrophilic and basophilic chemolithotrophs (mainly *Thiobacillus thioparus* and *Thiobacillus neapolitanus*) were found but also in low numbers (up to 10<sup>3</sup> cells ml<sup>-1</sup>). These bacteria are able to oxidize S<sup>0</sup> and soluble inorganic sulphur compounds but no sulphide minerals.

Paste pH was found strongly acidic, ranging between 1.8 and 2.5 (A and B samples respectively), indicating a high potential for acidic leachates generation and confirming the lack of inherent alkalinity producing minerals, as resulted from chemical analysis. Leaching of the samples with distilled water at 10% w v<sup>-1</sup> pulp density and room temperature in a 250 ml beaker for 4 hours caus-

Table 2. Acid Base Accounting

Waste	Total S (%)	MAP	NP		NNP	NP/MAP
			(kg CaCO <sub>3</sub> t <sup>-1</sup> sample)			
A	16.11	503.4	-40.4		-503.4	-0.08
B	11.10	347.2	-31.1		-347.2	-0.09

Table 3. Long term stability of the coal wastes, MEP (mg kg<sup>-1</sup>)

A	Fe	Mn	Pb	As	Zn	Cu	Cd
EP extract	8895	72	3.6	4.9	47	2.9	0.3
Stage 1	639	4.2	0.19	0.5	2.9	0.18	–
2	108	0.5	0.25	0.1	1.7	0.34	–
3	224	1.8	0.19	–	1.2	0.22	–
4	254	1.5	0.15	–	1.4	0.26	–
5	801	3.7	0.15	–	1.1	0.19	–
6	278	0.9	0.52	–	1.1	0.11	–

es solubilization of a number of phases and production of an acidic solution with the following characteristics: pH~2.0, concentration (mg l<sup>-1</sup>): Fe 1200-1700, Al 95-300, Mn 2-8, Cu 0.6-1.4, Ni 1.3-2, Co 1-1.4, Zn 10.7-19.7, Sr 0.5-2.7, Cr 0.1-0.4 and Pb 0.5-1.1. It is therefore concluded from this test that leaching of a number of hazardous constituents takes place under very mild conditions and very short periods of time.

Both samples exhibit extremely negative Net Neutralization Potential, ranging between -503 and -347 kg CaCO<sub>3</sub> t<sup>-1</sup> for A and B respectively, as seen in Table 2. These values, as well as the negative NP/MAP ratios, indicate that addition of considerable quantities of acid consuming materials, such as Ca-Mg carbonates, is required to inhibit the acid generation potential of the wastes, since the inherent neutralization potential of the wastes is very limited.

The long-term stability of sample A to acid leaching, as determined by the application of MEP technique is presented in Table 3. Sample B exhibits similar leaching characteristics.

Table 3 data indicate significant Fe and in lesser degree Zn and Mn leachability. Pb, As and Cd concentration in the extracts was found close or below the detection limits. Therefore, elevated

concentrations of manganese, iron and zinc are expected in the produced acidic leachates.

Toxic elements speciation, as determined by the application of sequential extraction procedure is presented in Table 4. It is seen from this data, that the bioavailability for a number of toxic elements such as Mn, Pb, Zn and Sb is high, since they are bound to mineralogical phases that can be easily attacked and leached by mild solutions. Solubilization of these elements and subsequent migration of the produced leachates contaminates surface streams and groundwater reservoirs. This probability is quite high, since in the areas under study numerous surface streams are seen and the water table is shallow.

TCLP results indicate that the wastes exhibit limited toxicity. Solubility varies between 1 mg l<sup>-1</sup> for Pb and 0.002 mg l<sup>-1</sup> for As, well below the regulatory limits set by US EPA. Limited solubilities are due to the nature of the leaching agent used in the TCLP test and its preferential attack on other waste constituents.

Interpretation of all laboratory experimental data reveals that Tula coal wastes exhibit characteristics that adversely affect the environment and therefore the risk at the disposal areas is considered high. They contain considerable amounts of



Table 4. Sequential Extraction Procedure (mg kg<sup>-1</sup> waste)

Element	Exchangeable-soluble fraction (MgCl <sub>2</sub> , pH=7)		Carbonate fraction (CH <sub>3</sub> COONa, pH=5)	
	A	B	A	B
Fe	5008	832	584.8	352.4
Mn	47.24	46.08	22.6	18.7
Pb	27.24	22.56	1	1
As	5	4	3	2
Sb	11.76	11.68	8.4	8.24
Zn	29.28	33.2	7.64	3.6
Cu	<0.8	<0.8	<0.8	<0.8
Cd	<0.3	<0.3	<0.3	<0.3

pyrite which is subject to oxidation and therefore production and migration of acidic leachates that may contaminate surface- and groundwater is expected to take place for a prolonged period. This conclusion is supported by the strong negative values of the net neutralization potential, the low paste pH, the lack of acid consuming minerals and the high exchangeable and carbonate fractions of several hazardous elements.

### EFFICIENCY OF DESULPHURIZATION TECHNOLOGIES

Desulphurization technologies, which are extensively applied for the removal of sulfur from coals prior to combustion, are broadly classified as physical, chemical, thermal or biological. Most of research work on coal waste desulphurization has been focused on pyritic sulfur removal, which represents in most cases at least half of the total sulfur content in coal, since organic sulfur is more difficult to be removed by conventional processes. Desulphurization aims mainly at breaking down the pyrite lattice and thus eliminating the acid generation potential of the wastes. The final desulphurized waste volume may be disposed of safely on the environment or used, if it possesses the required properties, as backfill in underground mining works.

Physical treatment includes flotation, magnetic separation or the use of hydrocyclones and mainly removes inorganic sulfur, whereas elimination of organic sulfur requires in most cases chemical and/or microbial treatment (Palmer *et al.*, 1995). Physical techniques, bearing in mind the nature

and the mineralogical characteristics of the coal wastes studied in this work, may involve flotation for the separation of pyrite, which represents a relatively small fraction of the total volume. Several studies have shown that pyrite can be removed (depressed) by flotation from un-oxidized cyanide free coal tailings by adding soda and increasing pH to approximately 11 (Benzaazoua and Bussiere, 1999). This rehabilitation option, by taking into account the volume of the wastes and the compaction caused after disposal, cannot be implemented *in situ* but it can be easily incorporated into an integrated coal management scheme for fresh tailings.

Chemical treatment involves the use of strong acids, bases or salts. It is usually applied at elevated temperatures, varying between 200 and 300 °C, and is characterized by limited selectivity. HNO<sub>3</sub> leaching at atmospheric pressure and elevated temperature (up to 90 °C) seems in some cases quite efficient achieving almost complete S removal (Rodriguez *et al.*, 1996). Leaching with sodium carbonate, sodium hydroxide or potassium hydroxide can be also effective, achieving 90% removal of both inorganic and organic sulfur (Lolja, 1999; Norton *et al.*, 1988). Although some of these techniques may be considered feasible, they are in general characterized by high cost and in addition neutralization of the produced effluents is required; only a limited number of these techniques can remove significant amounts of organic sulfur at low temperatures.

Leaching experiments, performed at the Lab. of Metallurgy of NTUA in glass stirred reactors with

HNO<sub>3</sub> and KOH at 10% w v<sup>-1</sup> pulp density and temperatures up to 80°C have shown that under the most intense conditions (80°C, 3N, 2h) maximum sulfur removal is limited and varies between 10% and 20%, while the overall weight loss reaches 35%. HNO<sub>3</sub> is a better leaching agent, compared to KOH, but the attained sulfur removal by no means is considered sufficient. Indeed, the acid generation potential of the wastes was reduced after treatment but still remained at values close to -100 kg CaCO<sub>3</sub> t<sup>-1</sup> of waste, indicating thus a noticeable remaining potential for CMD generation. Application of these techniques at elevated temperatures will definitely increase their efficiency, but due to a number of reasons this was not studied in the laboratory. The main reasons were (a) the limited selectivity of leaching, so that secondary treatment of the produced effluents is required in order to meet effluent discharge criteria and (b) the high cost and the operating difficulties envisaged when operating at high temperatures and corrosive environments. Therefore, by taking into account all these constraints, it is concluded that chemical leaching of Tula coal wastes, does not seem a feasible rehabilitation option.

Thermal treatment involves mainly pyrolysis (Lin *et al.*, 1997) or the use of air-steam mixtures. Both techniques operate at high temperatures (350-500°C), are considered quite complicated, require careful process and emission control and the degree of desulphurization varies depending on a number of parameters such as temperature, particle size, air-steam ratio/gas composition, coal rank, heating rate and type of reactor used (Sydorovych *et al.*, 1996). Since no large scale installations have been reported in literature for the thermal treatment of coal wastes, the feasibility of such techniques remains under question. Important parameters for the application of thermal treatment are the carbon and the ash content of the wastes, the additional heat sources required, the efficiency of the combustion devices (chamber furnace, fluidized bed etc.), the efficiency of the off-gases cleaning systems and the disposal of the produced ash. Several in situ waste treatment alternatives, such as "gaseous gasification" and "intradump gasification" have been patented in Russia, but no data from field applications is available.

Biological desulphurization is a well established laboratory technique that utilizes bacterial cul-

tures (thermophilic or mesophilic bacteria) to oxidise pyrite and therefore remove sulfur from coals (Gomez *et al.*, 1997). It may include the use of heap or reactor leaching (Moran *et al.*, 1997). Heap leaching, provided that disposal sites have been well prepared in terms of optimization of wetting, acidic solution circulation and collection of leachates produced, may prove efficient. Good selectivity of the bacterial cultures used (*T. Ferrooxidans*) may be attained, provided that they will be adapted to the operating environments in order to tolerate the presence of elements such as Mn, Sr and Se that are harmful in elevated concentrations (Komnitsas and Pooley, 1989; 1991). Attention should be paid though for the maintenance of the bacterial activity during the winter period in Russia and for the collection, neutralization and disposal of the produced effluents in order to prevent migration and subsequent groundwater contamination. In addition, the toxicity and stability of the resulting sludges, prior to disposal, should be examined with the application of standard tests. Finally, reactor leaching prior to disposal does not seem feasible at all, since the required retention times are expected to be quite long (1-2 weeks) resulting in high operating and maintenance costs. Despite the extent of research on biological desulphurization of different types of coal, there is hardly any attempt of applying the most successful and technically feasible options for the treatment of coal wastes. Several studies though, aiming at scale up design and process considerations, have stated that microbial depyritization can be effectively applied for the treatment of coal wastes (Olson, 1994; Moran *et al.*, 1997).

## CONCLUSIONS

Coal beneficiation wastes, disposed at the wider Tula area, Russia, constitute a serious environmental hazard since they are characterized by elevated content of pyrite, lack of acid consuming minerals and extremely negative net neutralization potential. These wastes are subject to oxidation, with the combined action of oxygen and bacterial activity, therefore acidic leachates with a very low pH and considerable concentration of hazardous elements are produced contaminating soils, surface- and groundwater and endangering the quality of the ecosystems at the Tula area. Due to a number of technological and environmental constraints, only a limited number of

desulphurization techniques seem feasible for *in situ* application. By taking into account the volume of the wastes, the characteristics of the site and the lack of similar previous large scale applications experience, it is understood that desulphurization techniques require considerable investment, operating and maintenance costs and careful process control, therefore their efficiency is under question. Some of them such as flotation, biological or thermal may prove feasible if incorporated into an integrated waste management scheme. Therefore, for the wastes examined in this experimental study other remediation technologies, including establishment of composite

covers, modification of the acid generation potential with the use of alkaline minerals or construction of barriers should be also considered, in order to inhibit oxidation of the sulphide phases, decontaminate the migrating leachates and protect the ecosystems at the affected areas.

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