

Kinetics of Metals Adsorption in Acid Mine Drainage Treatment with Blast Furnace Slag

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ABSTRACT This investigation employed granulated blast furnace slag as functional adsorbent to study adsorption phenomena in single and multiadsorbate systems of synthetic acid mine drainage containing Cu²⁺, Mn²⁺, Cd²⁺, Fe²⁺ and Co²⁺ ions. Batch experiments were conducted as function of initial pH, phase ratio, mixing time, slag particle diameter and initial metal concentration. The structure of slag was studied using various materials characterization techniques.

The efficiency and adsorption rates increased with decrease in particle diameter, decrease in initial metal concentration, increase in slag mass and increase in initial pH as expected. A high pH promotes adsorption possibly by precipitation and/or ion exchange processes. Interestingly, metal adsorption drastically reduced in multi adsorbates relative to single adsorbates. Pseudo second order model is most appropriate theory to satisfactorily describe experimental data. At high slag mass, coarse particle sizes and high initial concentration, film and intraparticle diffusion appear to limit adsorption based on Intraparticle model.

1 INTRODUCTION

1.1 Background

The uncontrolled natural oxidation of iron and sulphur compounds in mineral wastes generates Acid Mine Drainage (AMD) of typically low pH, high sulphates, heavy metals ions, etc that have polluted the environment worldwide (Akcil and Koldas, 2006; Skousen et al., 2000). Several (standard) treatment techniques exist for wastewater. Chemical precipitation, ion exchange, adsorption and membrane based filtration processes are among commonest (Fenglian and Wang, 2011). Traditionally, lime based chemical precipitation process is widely practiced to treat AMD (Akcil & Koldas, 2006; Kuyucak et al., 2001; Kuyucak, 2002; Robb and

Robinson, 1995). However, these chemicals are relatively expensive, kinetically slow and less efficient in the long term nature and effects of AMD (Barakat, 2011; Kuyucak, 2006; Robb & Robinson, 1995). A High Density Sludge (HDS) process (Kuyucak et al., 2001; Zinck, 2005) and engineered wetlands have been implemented on some mine sites (Kuyucak, 2006; Skousen et al., 1998).

Recently, several batch studies on the adsorption of heavy metal ions using iron/steelmaking slags and other industrial wastes as functional adsorbents have been published. Although they are yet to be understood in detail, it is believed that such materials may be sustainable alternative adsorbents to activated carbons and ion exchange resins (Ahmaruzzaman,

2011;Bailey 1999; Barakat, et al., 2011; Kurniawan et al., 2006; Sud et al., 2008). High metal adsorption capacity and efficiency involving slags in largely single and binary adsorbate systems have been reported, and the mechanisms of adsorption process and effects of process variables on metal adsorption have also been evaluated. Adsorbent capacity and degree of affinity were determined by fitting experimental data to the Langmuir and Freundlich adsorption isotherms (Curkovic et al., 2001;Dimitrova, 1996; Dimitrova, 2002; Dimitrova Mehandgiev, 2000; Dimitrova and Mehanjiev, 1998; Feng et al., 2004; Kim et al., 2008; Lopez et al., 1995; Lopez-Delgado et al., 1998). Though Xue et al (2009) studied multi-adsorption with basic oxygen furnace slag such studies are limited.

For silicate based materials such as slags, many authors believe metal adsorption process to occur through ion exchange and metal hydroxide/silicate precipitation (Dushina and Aleskovski, 1976), physical adsorption based on ion exchange (Lopez et al., 1995), predominantly sorption through ion exchange and some form of metal silicate precipitation (Dimitrova & Mehanjiev, 1998). In many instances, studies on the proposed mechanisms of metal adsorption with iron/steelmaking slags are limited, inconsistent and not yet clearly understood in many similar metal adsorption systems.

Kinetics of adsorption data is also necessary in order to determine rates of adsorption, residence time, etc needed in adsorption process design. Several kinetic models based on chemical and diffusion adsorption processes have been developed. Pseudo first and second order rate equations, Elovich rate equation, and liquid film and intra particle diffusion models have all been applied to analyse laboratory experimental data in general wastewater treatment (Ho and Mckay, 1998; Liu et al., 2010). As applied to slags Kim et al (2008) applied pseudo first order, pseudo second order and intra particle diffusion models to study Cu²⁺ adsorption on steelmaking slags (Kim et al., 2008). Ortiz et al (2001) applied first order model in Ni²⁺ adsorption with steel converter slags (Ortiz et al., 2001).

However, studies in multicomponent systems that reflect actual industrial effluent composition are limited and need to be conducted in order to understand kinetics and competitive metal adsorption phenomena. Further, there are very few reported studies that have employed kinetic models to study mechanism of metal adsorption with slags. This study investigated the adsorption efficiency and kinetics of Cd²⁺, Co²⁺, Cu²⁺, Fe²⁺ and Mn²⁺ ions using blast furnace slag adsorbent, as a function of slag (adsorbent) particle size, adsorbent mass, initial concentration and solution pH in single and multiadsorbate systems. The experimental data were then analyzed by fitting the data to common kinetic models in order to understand mechanisms of adsorption process and rate limiting factors involved.

2 MATERIALS AND METHODS

2.1 Slag Characterization

This investigation employed granulated blast furnace slag (BFS) from Tarmac Ltd UK as functional adsorbent to investigate the adsorption of heavy metal ions (Cu2+, Mn2+, Fe²⁺, Cd²⁺ & Co²⁺) from synthetic AMD solutions as described below. BF Slag particle size distribution was done by sieve analysis. An AutoPore IV 9500 V1.09 Micromeritics Mercury Porosimeter was employed to determine slag pore structure and pore size distribution. A Philips XL-30 Environmental Scanning Electron Microscopy (ESEM)-FEG fitted with an Oxford Inca 300 Energy Dispersive Spectroscopy (EDS) system was applied to pore structure, determine surface morphology and full chemical/elemental composition. The mineralogical chemical composition was also conducted by Siemens D5005 powder diffractometer (XRD) and Bruker S8 Tiger Wavelength Dispersive X-Ray Spectrometer physical (XRF) respectively. Other properties such as specific surface area was

done by Nitrogen adsorption fitted to BET Equation and density by AccuPyc II 1340 V1.05 Micromeritics Helium gas Pycnometer. The results are discussed in sections that follow.

2.2 Stock and Synthetic AMD Solutions

Standard stock solutions of 1000 mg/L Cu^{2+} , Mn^{2+} , Fe^{2+} , Cd^{2+} & Co^{2+} ions were prepared separately from their respective analytical grade chemicals (CuSO_{4.5}H₂O₅) MnSO₄.4H₂O, FeSO₄.7H₂O, 3CdSO₄.8H₂O & CoSO₄.7H₂O) from Fisher Scientific UK using distilled water. Subsequent AMD solutions of different metal concentrations were prepared by appropriate dilutions of stock solutions, which simulated average compositions of actual AMD solutions of a worked out (old) Chibuluma copper/cobalt Mine of Zambian Copperbelt mining operation. The pH was adjusted manually using 1.0 mol/L NaOH or conc. H₂SO₄ solutions.

2.3 Experimental Procedure

Batch adsorption experiments conducted in ½ litre capacity plastic bottles with tight screwed caps agitated on a tumbling mill, as function of pH (1.50, 3.50 & 5.50), phase ratio or mass of slag to aqueous volume (2-10% w/v slag), mixing time (3-6 hours), slag particle diameter (dp < 45 µm & 0.18-1.00 mm size fractions) and initial metal ion concentration (20-300 mg/L). The required initial metal ion concentration from stock solutions were added to the ½ L capacity plastic bottles, after pH was adjusted to the required value with a bench HI 2211 pH meter. The required mass and particle size fraction of slag (as received) was then added, placed onto tumbling mill and agitated at 110 rpm for a predetermined time period. 20 mL slurry sample aliquots were periodically taken and filtered. Equilibrium metal concentrations were measured on the filtrate by Flame Atomic Absorption Spectrometer (Perkin Elmer AAnalyst 300) from which efficiency (η) and adsorption capacities (Q)

were calculated by equations (1) and (2) helow.

$$Q_t = \frac{\left(C_o - C_t\right) * V}{m} \tag{1}$$

$$\eta = \frac{(C_o - C_i)}{Co} * 100\%$$
 (2)

Where Q_t (mg/g) = adsorbate concentration at any time t; C_o , C_t (mg/L) = initial adsorbate concentration and at any time t (min) respectively; m (g) = mass of adsorbent; V (L) = Volume of solution.

3 RESULTS AND DISCUSSION

3.1 Slag Physical and Chemical Properties

Table 1 below gives the oxide composition of granulated blast furnace slag as determined by XRF. The high lime (44% CaO) content means that the material has a potentially high neutralizing capacity for acidic effluents. The specific role of each of these components in adsorption is subject to further study.

However, the XRD pattern did not detect the presence of any crystalline mineral phases suggesting that the slag is highly amorphous.

Table 1: Properties of BF slag

Chemical		Physical			
composition		properties			
Oxide	% w/w	Parameter	Value		
CaO	44.1	BET surface area	$0.769 \text{ m}^2/\text{g}$		
SiO ₂	30.7	True density	2.89 g/cm ³		
Al_2O_3	10.6	Particle dia dp	dp < 45 μm		
MgO	5.8	Porosity	54.5%		
TiO ₂	0.74	Total pore vol	0.426 mL/g		
K ₂ O	0.62	Total pore area	$1.275 \text{ m}^2/\text{g}$		
MnO	0.71	Average pore dia	1.336 μm		
Fe ₂ O ₃	0.39				
Na ₂ O	0.27				
BaO	0.21				
SO ₃	1.98				

3.1.1 Pore size distribution

The pore size distribution is shown in Figure 1 from which it can be deduced that pore sizes are greater than 50 nm, hence the material is macroporous. Other characteristic Porosimetry parameters of slag are shown in Table1.

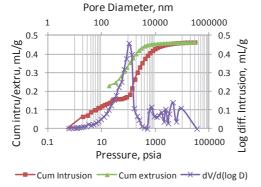


Figure 1: Pore size distribution of blast furnace slag for 0.18 < dp < 0.36 mm slag size fraction.

3.1.2 SEM Surface morphology

Figure 2 below is an Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) showing macroporosity surface structure with elemental composition

From EDS analysis of slag surface Ca²⁺, Mg²⁺, K⁺ & Na⁺ are potentially exchangeable cations, thus heavy metals could be removed from solution by ion-exchange process.

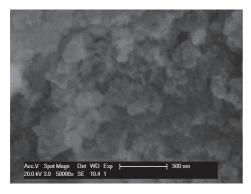


Figure 2: SEM-Energy Dispersive Spectroscopy (EDS) nanostructure for 0.18 < dp < 0.36 mm slag size fraction.

3.2 Adsorption Kinetics and Efficiency

3.2.1 Kinetic Modeling

Rate of adsorption is controlled by (1) external (or film) diffusion across liquid film surrounding adsorbent particles, (2) intra particle (or internal or pore) diffusion in the internal pore sites or walls of adsorbent particles and (3) sorption which may involve one or several mechanisms, e.g., physisorption, chemisorption, ion exchange, precipitation, complexation etc (Qiu et al., 2009).

In this study pseudo first order, pseudo second order and Elovich's rate equations based on chemical adsorption as well as intra particle diffusion model were applied to the experimental data in order to analyze the rate limiting steps and infer the mechanisms of metal adsorption under various solution and experimental conditions.

3.2.1.1 Pseudo first order model

Lagergren pseudo first order rate equation (Ho & Mckay, 1998) is defined as

$$\frac{dQ_t}{dt} = k_1 (Q_e - Q_t) \tag{3}$$

Equation (3) is integrated (t = 0 to t = 0 and $Q_t = 0$ to $Q_t = Q_t$) and expressed in linear form as

$$\log(Q_{e} - Q_{t}) = \log(Q_{e}) - \frac{k_{1}}{2303}t \tag{4}$$

Where (Q_t, Q_e) = amount of metal ions adsorbed per unit weight of adsorbent (mg/g) at any time t (min) and at equilibrium respectively, k_1 is adsorption constant (mg/g) min).

If the model applies, a plot of log (Q_e-Q_t) vs. t should be linear.

3.2.1.2 Pseudo second order rate Model

Pseudo second order (PSO) kinetic model is given by the differential equation (Ho, 2006;Ho & Mckay, 1998;Ho and Mckay, 1999;Qiu et al., 2009) as;

$$\frac{dQ_t}{dt} = k_2 (Q_e - Q_t)^2 \tag{5}$$

Where (Q_t, Q_e) = amount of metal ions adsorbed per unit weight of adsorbent (mg/g) at any time t (min) and at equilibrium

respectively, k_2 is adsorption constant (mg/g min).

Integrating equation (4) (between t = 0 to t = t and $Q_t = 0$ to $Q_t = Q_t$ to linear form gives;

$$\frac{t}{Q_{i}} = \frac{1}{kQ_{e}^{2}} + \frac{1}{Q_{e}}t \quad or \quad \frac{t}{Q_{i}} = \frac{1}{h} + \frac{1}{Q_{e}}t \tag{6}$$

 $h = kQ_e^2$ = initial adsorption rate (mg/g min) as t goes to zero. Thus, Q_e , k and h can be determined experimentally from the slop and intercept of linear plots of t/Q_t vs. t

3.2.1.3 Elovich's model

The differential equation (Ho, 2006) is given as

$$\frac{dQ_t}{dt} = a e^{-\alpha Q_t} \tag{7}$$

The integrated (t=0 to t=0 and $Q_t=0$ to $Q_t=Q_t$) and linearised form is

$$Q_{t} = \left(\frac{2.3}{\alpha}\right) \log(t + t_{o}) - \left(\frac{2.3}{\alpha}\right) \log t_{o}$$
 (8)

Equation (8) was simplified on assumption that $a\alpha t >> 1$ to give a linear equation (9);

$$Q_t = \alpha \ln(a\alpha) + \alpha \ln(t) \tag{9}$$

Where a = desorption constant (g/mg), α = initial adsorption rate (mg/g min), $t_o = 1/(\alpha a)$, Q_t = amount of metal ions adsorbed per unit weight of adsorbent (mg/g) at any time t (min)

A plot of Q_t vs. ln(t) gives a straight line from which the parameters are obtained.

3.2.1.4 Weber-Morris Intraparticle diffusion model

The rate expression for intra particle diffusion limited adsorption process as presented by Weber and Morris (Qiu et al., 2009) is

$$Q_t = k_i \sqrt{t} \tag{10}$$

 Q_t = amount of metal ions adsorbed per unit weight of adsorbent (mg/g) at any time t (min), k_i = intra particle diffusion rate constant (mg/g min^{-1/2}), t = time.

A plot of Q_t vs. t^{-1/2} should be linear if intra

A plot of Q_t vs. t^{1/2} should be linear if intra particle diffusion is the rate determining step (RDS) of the process. Where the line intercept is not zero, the process could be accompanied by film diffusion.

Kinetic modeling results are presented in sections that follow.

3.2.2 Single adsorbate system

3.2.1.1 Effect of particle size

Batch bottle-rolling experiments using $\frac{1}{2}$ Litre bottles agitated at 110 rpm were conducted in single and multicomponent adsorption systems with four different size fractions of BF slag, i.e., dp < 45 \mum, 0.18 < dp < 0.36 mm, 0.36 < dp < 0.50 mm and 0.50 < dp < 1.00 mm. Unless stated otherwise, all experiments were conducted at a slag dosage of 3g per 100 ml of synthetic AMD with initial concentration of each adsorbate at 100 mg/L and initial pH of 3.50 at 20 °C.

adsorption increased with a Metal decrease in particle diameter of slag due to increase in surface area. This increases the adsorption opportunity on outer slag surfaces. The initial rates of adsorption were rapid probably because of (1) high mass transfer rates based on high concentration gradient of adsorbates that drives diffusion flux across the film boundary layer into slag pores, and (2) high availability of active adsorption sites. Adsorption rate later decreased with time, as expected, because free adsorption sites and concentration gradient decreases. As for $dp < 45 \mu m$ size fraction, adsorption was nearly instantaneous and complete (100%) for all metal ions under the conditions employed (bottle roller at 110 rpm, 5% w/v BFS, 100 mg/L Me²⁺, pH 3.50 at room temp.). For coarser size fractions, highest adsorption efficiency (100% Fe²⁺, Cu^{2+} & Cd^{2+} ; 87% Co^{2+} , 57% Mn^{2+}) were obtained with 0.18 < dp < 0.36 mm finest size fraction as given in Figure 3 below. Mass transfer resistance is high for larger particles (Ahmaruzzaman, 2011). Efficiency of adsorption was high and selective towards Fe²⁺ and Cu²⁺ but moderate towards Cd²⁺ and low for Co²⁺ and Mn²⁺. Co²⁺ and Mn²⁺ adsorption is low that probably require longer residence time under these conditions. adsorption preference $Fe^{2+}>Cu^{2+}>>>Cd^{2+}>>Co^{2+}>Mn^{2+}$.

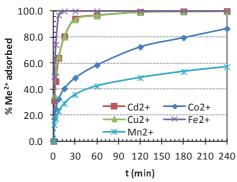


Figure 3: Metal (Me^{2^+}) adsorption vs. time in single adsorbate system at initial pH_o 3.50, 3% w/v BF Slag, 97±6 mg/L Me^{2^+} , 0.18<dp<0.36 mm size fraction, 20°C.

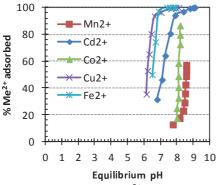


Figure 4: Metal (Me^{2+}) adsorption vs. equilibrium pH in single adsorbate system at initial pH_o 3.50, 3% w/v BF Slag, 97 ± 6 mg/L Me^{2+} , 0.18<dp<0.36 mm size fraction, 20° C.

From Figure 4, variation of equilibrium pH is different for all metals at same experimental conditions. This might be helpful in assessing selective metal adsorption based on initial pH in a multiadsorbate system.

Based on the theoretical solubility of metal hydroxides as function of pH and metal concentration, observed experimental metal ion concentrations against equilibrium pH suggests metal removal to involve metal hydroxide precipitation for Cu²⁺ and Fe²⁺ except probably Cd²⁺, Mn²⁺ and Co²⁺ for which precipitation may be negligible. The precipitation model reaction is given in equation 13 below. However, it has been reported that adsorption process is kinetically

much faster than chemical precipitation of metal hydroxide (Gao et al., 1995).

Four kinetic models (See section 3.2.1) were applied to test whether metal adsorption was controlled by diffusion or chemisorption. The results for linear data fit to pseudo second order model (PSO) in single adsorbates are shown in Figure 5 using 0.18 < dp < 0.36 mm particle size fraction.

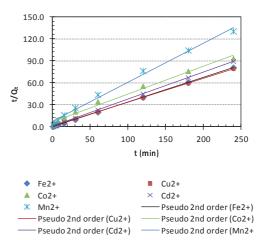


Figure 5: Linear plots of t/Q_t vs. t for pseudo second order kinetic model for single adsorbates at pH_o 3.50, 3% w/v BF Slag, 97±6 mg/L Me²⁺, 0.18 < dp < 0.36 mm size fraction, 20°C.

Values of initial adsorption rates (h) and rate constant (k) from PSO increased with decrease in particle size diameter. However, Q_e was more sensitive to slight variation in initial metal concentration than particle size diameter. This observation and based on high values of regression coefficient ($r^2 > 0.99$) from linear plots of PSO (Fig. 5), chemisorption may be rate limiting.

Lagergren's pseudo first order model was applicable up to about 15 minutes at best, and therefore the results are not shown here.

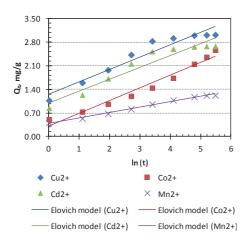


Figure 6: Linear plots of Q_t vs. ln(t) for Elovich kinetic model for single adsorbates at pH_o 3.50, 3% w/v BF Slag, 97 ± 6 mg/L Me^{2+} , 0.18 < dp < 0.36 mm size fraction, $20^{\circ}C$.

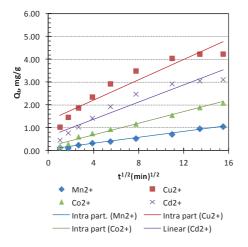


Figure 7: Linear plots of Q_t vs. $t^{1/2}$ for Intra particle diffusion kinetic model for single adsorbates at pH_o 3.50, 3% w/v BF Slag, 97 ± 6 mg/L Me²⁺, 0.18 < dp < 0.36 mm size fraction, 20° C.

Figures 6 and 7 above depict linear fits of the Elovich and Intraparticle diffusion models ($r^2 > 0.950$). For the intraparticle model, the straight lines do not pass through the origin to suggest that both film and intraparticle diffusion may be limiting.

3.2.1.2 Effect of Initial pH

Solution pH controls several variables that include speciation of metal ions and surface charge density of adsorbents. At unique pH values, different solids posses different values of points of zero charge (PZC) above which adsorption may increase or decrease depending on oxidation state of metal ions and electrostatic repulsion (Huang and Rhoads, 1988; Ortiz et al., 2001; Feng et al., 2004). In the Figure below, it was observed that an increase in initial pH increased efficiency (%) and rate of metal adsorption as well as adsorption capacity. The results supports the fact that metal adsorption on silicate based materials (slags) is only effective in alkaline solution (Huang and Rhoads, 1988). However, adsorption was practically negligible at pH 1.50 largely due to the competitive effect of H⁺ adsorption (Gao et al., 1995) and electrostatic repulsion (Feng et al., 2004) between metal ions and surface charges. Metal adsorption was accompanied by gradual increase in equilibrium pH due to slag hydrolysis (Dimitrova and Mehandgiev, 2000).

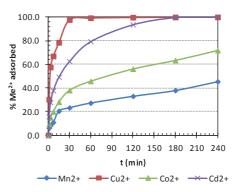


Figure 8: Metal (Me^{2^+}) adsorption vs. time in single adsorbate system at initial pH $_{\rm o}$ 5.50, 3% w/v BF Slag, 97±6 mg/L Me $^{2^+}$, 0.50<dp<1.00 mm size fraction, 20°C.

BF slag is based on a silicate frame work that undergoes hydrolysis to support ion exchange and other sorption processes. Depending on pH and metal ion concentration, hydroxide or silicate precipitation and coprecipitation may be

involved (Dimitrova, 2001; Dimitrova and Mehandgiev, 2000). From SEM/EDX analysis of slag surface and observed alkaline equilibrium pH values, it is possible that ion exchange process and adsorption may contribute to overall Mn²⁺, Co²⁺ and Cd²⁺ adsorption due to the presence of exchangeable cations (Ca²⁺, K⁺, Na⁺, etc) on slag surfaces. As for adsorption of Fe²⁺ and Cu²⁺ ions, probably ion exchange, adsorption and precipitation may be the major mechanisms of adsorption as proposed in several studies (Dimitrova, 1996; Dimitrova and Mehandgiev, 1998, 2000; Feng et al., 2004; Kim et al., 2008).

A simplified ion exchange and precipitation processes (Dimitrova, 2001; Dimitrova and Mehandgiev, 2000; Gao et al., 1995) on protonated or unprotonated negative slag surface site (Al, SiO⁻) is given in Equations (11-13) below;

$$\overline{(\equiv SO)_{2}^{-}}Ca^{2+} + Me^{2+}(aq) \Leftrightarrow \overline{(\equiv SO)_{2}}Me^{2+} + Ca^{2+}(aq) \quad (11)$$

Where overbar = solid phase, $\equiv SO^-=$ deprotonated surface site, S = Al, or Si; Me²⁺ = any metal ion.

In strongly acidic solutions, competitive adsorption is represented by;

$$(\equiv SO)_{2}^{-}Ca^{2+} + Me^{2+}(aq) + H^{+}(aq)$$

$$\Leftrightarrow (\equiv SO)_{2}H^{+} + Me^{2+}(aq) + Ca^{2+}(aq)$$
(12)

Slag hydrolysis produces OH which may result in hydroxide precipitation as;

$$Me^{2+} + OH^{-} = Me(OH)_{2}$$
 (13)

3.2.3 Multi Adsorbate system

3.2.1.1 Effect of particle size

Two particle size fractions of BFS were investigated, i.e., dp < 45 μ m and 0.18 < dp < 0.36 mm in a multiadsorbate synthetic wastewater of Cd²⁺, Co²⁺, Cu²⁺, Fe²⁺ and Mn²⁺ at about 100 mg/L each at same experimental and solution conditions as in single adsorbates (pH_o 3.50; 3% w/v BF Slag). Interestingly, % metal adsorption drastically reduced in multi adsorption relative to single adsorbates, that is, from 100 to 18% Cd²⁺, 87 to 7.6% Co²⁺, 100 to 96% Cu²⁺, 57% to negligible value for Mn²⁺

but Fe²⁺ was unaffected at 100%. Xue et al (2009) obtained similar results in Cu²⁺, Cd²⁺, Pb²⁺ and Zn²⁺ adsorption with basic oxygen furnace (BOF) slag. This observation might be attributed to the competitive adsorptive effect among metal ions for the same (available or free) adsorption sites and several other factors that may be at play such as differences in slag's pore sizes relative to that of metal ionic radii, differences in element electronegativities, high affinity of slag for specific metal ions (Fe²⁺ & Cu²⁺) and probably a general limitation in the material's adsorptive properties (low specific surface area, porosity, etc).

Adsorption rates and capacity increased in a multi adsorbate system when a very fine size fraction (dp < 45 μ m) of slag was employed. Though adsorption was 100% in all single adsorbates, this was limited to 62% Mn^{2+} and 84% Co^{2+} with 100% for Fe^{2+} , Cu²⁺ and Cd²⁺ in a multi adsorbate system (Fig.3). Therefore, of the two size fractions, better adsorption results were obtained for dp < 45 µm size fraction for all metal ions. Again, Co²⁺ and Mn²⁺ adsorption is slow that require longer residence time under these conditions. However, adsorption of Co²⁺ and Mn²⁺ improved when the feed concentration was reduced to 50 mg/L at same experimental conditions but final solution concentration (0.60 mg/L Co²⁺ & 4.53 mg/L Mn²⁺) were still higher than the permissible discharge limits. [15] inally at 20 mg/L all metals were completely removed from multi adsorbate solution. Thus, an optimum particle size diameters and adsorbent mass in relation to initial feed concentration of metal ions is expected to work effectively in dilute solutions.

Again, Figures 9 and 11 below depict linear fits of the Elovich and Intraparticle diffusion models with $\rm r^2>0.950$ in multiadsorbates. As before, for the intraparticle model, the straight lines do not pass through the origin to suggest that both film and intraparticle diffusion may be probably limiting.

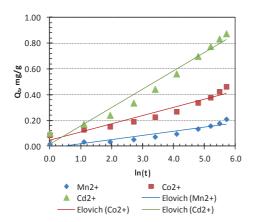


Figure 9: Linear plots of Qt vs. ln(t) for Elovich kinetic model for multi adsorbates at pHo 3.50, 3% w/v BF Slag, 97±6 mg/L Me2+, 0.18 < dp < 0.36 mm size fraction, 20oC.

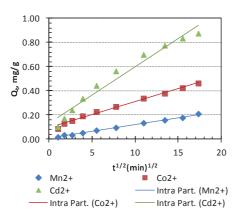


Figure 11: Linear plots of Q_t vs. $t^{1/2}$ for Weber-Morris Intra Particle kinetic model for multi adsorbates at pHo 3.50, 3% w/v BF Slag, 95 ($\pm 8\%$) mg/L Me²⁺, 0.18 < dp < 0.36 mm size fraction, 20°C.

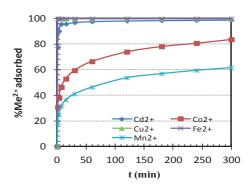


Figure 10: % Metal (Me^{2^+}) adsorption vs. time (min) in multi adsorbate system at initial pH_o 3.50, 3% w/v BF Slag, 97 ± 6 mg/L Me^{2^+} , dp < 45 μ m size fraction, room temp (20° C)

3.2.1.2 Effect of adsorbent mass

The efficiency, rates and capacity of adsorption for all metal ions studied increased with increase in mass of adsorbent. This is to be expected since available adsorption surface area and hence adsorption sites increase. Figure 12 below shows Cd^{2+} adsorption as a function of mass of slag. From Weber-Morris intraparticle diffusion model, adsorption was increasingly limited by film and intraparticle diffusion processes as mass of adsorbent increased. Effect of diffusion limitation for Fe^{2+} and Cu^{2+} was negligible.

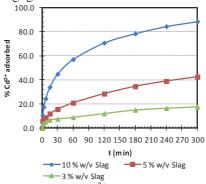


Figure 12: % Cd^{2+} adsorption vs. time in multi adsorbate system at initial pH $_{\rm o}$ 3.50, 3% w/v BF Slag, 97±6 mg/L Me $^{2+}$, dp < 45 μ m size fraction, 20°C.

3.2.1.3 Effect of initial concentration

An increase in initial metal ion concentration increased the equilibrium adsorption capacity but decreased the efficiency of adsorption. Mn²⁺ adsorption at different initial concentration is shown in Figure 13 below. A high concentration gradient provides the necessary driving force to overcome mass transfer resistance.

Adsorption decreased with increase in initial concentration for Cd²⁺, Co²⁺ and Mn²⁺, but Cu²⁺ and Fe²⁺ adsorption was not affected within the concentration range investigated (20-300 mg/L). However, adsorption was 100% at low concentration (20 mg/L) for all adsorbates.

Based on pseudo second order kinetic model parameters and regression coefficients $(r^2 > 0.995)$ from fitting experimental data, chemisorptions is largely the rate limiting process for metal ions that exhibited low adsorption, and this was supported by Elovich model fit $(r^2 > 0.950)$.

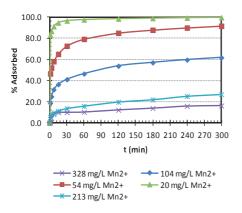


Figure 13: % Mn^{2+} adsorption vs. time in multi adsorbate system at initial pH_o 3.50, 3% w/v BF Slag, 97 ± 6 mg/L Me^{2+} , dp < 45 μm size fraction, $20^{\circ}C$.

4 CONCLUSION

This study has established that the efficiency and adsorption rates increased with decrease in particle diameter, decrease in initial metal concentration, increase in slag mass and increase in initial pH as expected. A high pH promotes adsorption possibly by

precipitation and/or ion exchange processes. Interestingly, % metal adsorption drastically reduced in multi adsorbates relative to single adsorbates, i.e., from 100 to 18% Cd²⁺, 87 to 7.6% Co^{2+} , 100 to 96% Cu^{2+} , 57% to negligible value for Mn^{2+} but Fe^{2+} was unaffected at 100%. This was attributed to competitive adsorptive effect and perhaps a limitation in the slag adsorptive properties. More studies are underway to understand multiadsorption systems. It was shown that pseudo second order model is the most appropriate theory to satisfactorily describe experimental data, supported by Elovich model. These models predict chemisorption to be the rate limiting step. However, high mass of slag, high initial metal ion concentration and coarse particle sizes, both film and intraparticle diffusion processes, in addition to chemisorption, appear to limit based Weber-Morris adsorption on Intraparticle diffusion model.

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Hydrogeotechnical and Geochemical Characterization of Surface Paste Tailings Disposal

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ABSTRACT This paper presents the results of a field cell testing undertaken to study the effect of in situ conditions on behaviour of sulphidic paste tailings. Tailings were deposited in thin layers (10 layers of 10 cm each one) into two cells $(D \times L \times H = 8 \text{m} \times 15 \text{m} \times 2 \text{m})$ which represent cemented (CC) and uncemented (UC) configurations. 2 wt% of cement was added in the first layer of the cell to study its effect; the second cell is cement-free. Results show that the CC provides slightly higher volumetric water content and smaller suction values than the UC, showing a capillary barrier cover of cemented layer which keeps the paste moisture and highly saturated ($S_r > 85\%$). Such a high S_r also confirms that there does not exist any oxygen transport between layers and limits or even eliminates acid generation.

1 INTRODUCTION

The increased environmental liabilities that go along with traditional tailings placement strategies mean that new and existing mines need alternative tailings deposition methods that more efficiently meet environmental and regulatory requirements (Aubertin et al., 2002; Bell and Donnelly, 2006; Bussière, 2007; Benzaazoua et al., 2008; Blight, 2010). One of these emerging techniques is surface paste disposal (SPD), where each layer of dewatered tailings is deposited and allowed to dry before the next layer is put in place.

The SPD becomes an attractive option to conventional tailings management methods, since it allows for a smaller tailings footprint area, increased water recovery capabilities and lower environmental impacts (Grabinsky et al., 2002; Verburg, 2002; Cadden et al., 2003; Bussière et al., 2004; Benzaazoua et al., 2004; Simms et al., 2007; Deschamps et al., 2007, 2008; Bryan et al., 2010). Many studies have been conducted to understand a number of aspects related to the behaviour of the SPD at laboratory and field scales. These include rheological behaviour for a superior tailings delivery system, and depositional

behaviour in order to lessen environmental impact and improve geotechnical properties (Theriault et al., 2003; Theron et al., 2005; Oxenford and Lord, 2006; Verburg et al., 2006; Simms et al., 2007; Deschamps, 2009; Martin et al., 2010). The behaviour of SPD has also been examined using the laboratoryscale physical models, which could simulate the real in situ surface deposition conditions in terms of consolidation, volumetric change, evaporation, cracks, climatic conditions, and geometry (Kwak et al., 2005; Landriault et al., 2007, 2001; Deschamps et al., 2011; Henriquez and Simms, 2009; Deschamps, 2009). These works show that field testing is indispensable to completely understand the behaviour of SPD. However, the physical models developed provide promising results and important insight into the deposition mechanisms by which precipitation and/or evaporation may become key factors in the occurrence of cracks observed on the top surfaces of paste tailings, and consequently in evaluating the mid-and long-term tailings disposal performance and quality.

Hence, a full knowledge of these aspects is needed to evaluate in situ placement and depositional behaviour of paste tailings to further improve an efficient waste disposal configuration or strategy. In this view, this paper presents the preliminary results of the field testing undertaken for assessing the field performance of SPD at LaRonde mine (Canada). The work focuses mainly on a conceptual design and construction of field cells with specific instrumentation, and on a field testing and monitoring program. The aims of this work are; i) to assess the effect of two different depositional configurations (locally cemented cell - CC and uncemented cell - UC) on surface paste tailings disposal; ii) to better characterize the behaviour and properties of paste tailings over time; and iii) to produce some helpful findings that can be used for a tailings management system at the LaRonde site. The key interest of the present paper stems in part from the fact that this is one of the very first attempts, to the authors' knowledge, to investigate in situ behaviour of paste tailings under accurately simulated surface disposal conditions.

2 MATERIAL AND METHOD

2.1 Material

The sulphide-rich, and filtered paste tailings were sampled as representative of the tailings streams from the paste plant of the LaRonde polymetallic mine (Au-Ag-Zn-Cu), located in Abitibi area (Quebec, Canada). Portions of the samples were air dried to conduct a set of laboratory tests needed for characterization of the samples. The following lab tests were conducted according to American Society of Testing Materials (ASTM) standards testing procedures. Tests were done in triplicate and their average values are reported. Further details on material properties can be found Yilmaz (2010), and Yilmaz et al. (2011).

2.1.1 Physico-Chemical Properties

The grain size distribution (Figure 1) results show that most of the grain size falls into the silts to fine sand range, containing a slight clay-sized particle of 3.5%. The fine content (< 20μ m) in paste tailings was 41 wt%. The effective particle diameter D_{10} within tailings was 5μ m. The coefficients of uniformity (D_{60}/D_{10}) , curvature $[(D_{30}^2/D_{60}\times D_{10})]$ and

gradation $[(D_{90}-D_{10})/D_{50})]$ for tailings were respectively determined as 6.9, 1.0 and 5.2. Paste tailings have a water content of 24.3% and a solids specific gravity of 3.4.

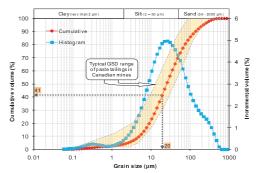


Figure 1. Cumulative and incremental GSD curves of paste tailings

The binding agent has a specific gravity of 3.15, a specific surface area of 1.58 m^2/g , a Al_2O_3 content of 4.86 wt%, a CaO content of 65.76 wt%, a Fe₂O₃ content of 2.44, and a SiO_2 content of 19.51 wt%.

Tailings samples' chemical analysis shows that sulphate content was relatively high at 3295 ppm due to a cyanide destruction process using SO₂/Air method. The calcium content was high at 505 mg/L, presumably due to the addition of lime for pH control during milling. Given that the acidification potential AP of 897.2 kg $CaCO_3/t$ (AP = $31.25 \times S_{sulphide}$), tailings are acid generating. Table 1 lists a summary of geochemical properties of tailings. Oxydo-redox potential was measured using a Pt/Ag/AgCl electrode and then converted to the standard hydrogen electron potential.

Table 1. Geochemical properties of tailings

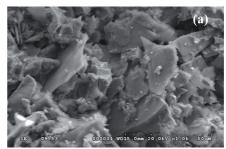
Parameter	Value
Sulphate content (ppm)	3295
Calcium content (mg/L))	505
Acidification potential (kg CaCO ₃ /t)	897.2
pH (hydrogen ions)	9.05
Oxydo-redox potential (mV)	156
Electrical conductivity (mS/cm)	8.24

2.1.2 Mineralogical Properties

Results revealed that tailings were dominated by quartz (53 wt%) and pyrite (28.7 wt%).

Minor quantities of alumino-silicate minerals such as paragonite (6.7 wt%), muscovite (4.9 wt%), chlorite (4.7 wt%), and gypsum (2.1 wt%) were well detected. Figure 2 presents the XRD profile of paste tailings, indicating the contents of major elements. Considering the water retention potential of silicates and the sulphate generation potential of iron sulphides, the studied tailings may affect the short- and long-term performance of surface paste disposal technique.

To identify the chemical composition of the mineral phases, the scanning electron microscope coupled with energy dispersive X-ray spectroscopy (SEM-EDS) analysis was done and the obtained results are shown in Figure 3. SEM-EDS results confirm that sulphur (18.4%S) and iron (23.1%Fe) leading to sulphide oxidation and sulphate production were the main two elements in tailings, as indicated earlier by chemical and mineralogical analyses. Silicon (13.5%Si) and aluminum (5.2%Al) precipitate within tailings as stable hydroxides while calcium (1%Ca) precipitates as expansive gypsum.



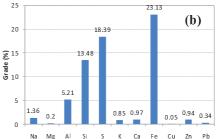


Figure 3. SEM micrograph (a) and EDS analysis (b) of paste tailings

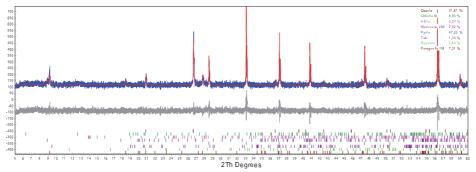


Figure 2. Typical X-ray diffraction profile of paste tailings

2.1.3 Microstructural Properties

Results are shown in Figure 4. MIP results show that the total porosity n_{tot} is 48.6% for uncemented tailings and 45.4% for tailings with 2 wt% cement. Critical pore diameter d_{cr} was respectively 0.5 µm and 1.3 µm for uncemented and cemented paste tailings. The observed difference between cemented and uncemented tailings justifies an evolution of texture and pore structure as a function of the binder used and its hydration (as pores are filled by hydrates or precipitates).

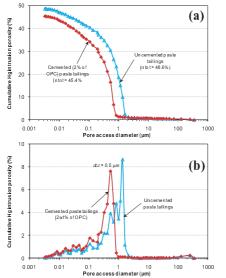


Figure 4. Cumulative (a) and incremental (b) PSD curves of paste tailings

2.2 Method

2.2.1 Conceptual Design

Two cells were designed at the mine to be exposed to natural atmospheric conditions. Each cell was built with a basement that consists mainly of tailings slurry deposited according to conventional mode (60-70 cm thickness) and self-weight consolidated during 10 months before layer by layer paste disposal. The first cell is designed by filling one layer with tailings containing a cement rate of 2 wt%, named in this paper cemented cell – CC while the second cell is designed by filling completely with tailings without cement and named uncemented cell – UC.

The UC is also considered as a control cell. Paste tailings are deposited in thin layers (10 cm). Each cell contains 10 paste layers and is designed to have a storage capacity of 90-95 m³ of paste tailings. The angle of deposition of the slope was kept as 30°. Paste tailings were produced in the paste plant after destruction of cyanide and delivered to the site through a ready-mix truck. To get flat surfaces in each layer, the paste materials are adjusted manually during placement. In terms of geometry, the cell

(Figure 5) was designed as an inverted pyramid, with a basal area $(8.1 \times 2 \text{ m} = 16.2 \text{ m}^2)$ and a top surface area $(15 \times 7.9 \text{ m} = 118.5 \text{ m}^2)$. Paste layers were filled parallel to the basal surface of pyramid cells to control the thickness of each paste layer. The tailings slump value was at least 250 mm (measured by the Abrams slump cone), corresponding to a pulp density (solid content) of 75 wt%.

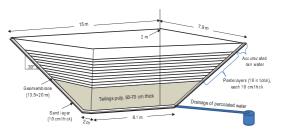


Figure 5. Cumulative and incremental GSD curves of paste tailings

Currently, the placed paste tailings are uncovered and thus are exposed to air and precipitation in the existing tailings pond. To simulate the in situ disposal condition, a thin layer (at a 60-70 cm thickness) of similar tailings pulp discharged to the tailings ponds is primarily poured into the cells, following the remaining ten layers of paste, and no soil cover or other covers are placed on top of the cells, as it is practiced at the current mine tailings ponds. Accordingly, oxygen and rainfall can contact the materials filled in the cells directly.

2.2.2 Field Cell Construction

The testing site selected for construction of two field experimental cells is just near the existing tailings pond at LaRonde mine.

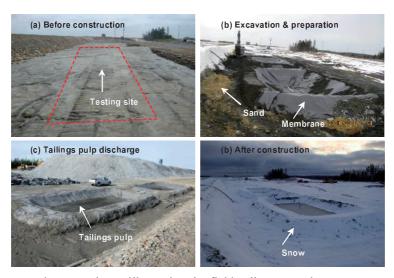


Figure 6. Photos illustrating the field cell construction steps

Figure 6 shows the testing site before and after construction, taking into account the preparation stages of sand, geo-membrane and tailings pulp. An area of rectangles of 15 m × 7.9 m for each field cell is dug by a mechanical mini excavator. To ensure proper drainage of water percolated during filling and/or after the rain, the basal surface area is slightly tilted by an angle of 1°, confirmed by theodolite. Following the excavation, local inert sand with a respective grain size (d_{15}) of less than 0.4 mm is used to simulate drainage conditions. Background and cell walls are coated with a layer of sand (10 m³). The ground surface is then compacted with a vibrating plate to reduce the permeability. A high-flow drainage geomembrane is inserted for protection against soil damage. To avoid any leakage of water from basin, bentonite is also added to the contact periphery between the pipe and the membrane. Tailings slurry (at 55 wt% solids) is pumped directly from the tailings ponds into the cells and left to self-weight consolidate for a time period of 10 months to copy the existing tailings pond, and to create the starter embankment in the cells before subsequent raises.

The paste materials prepared at the paste backfill plant at mine are delivered by using a ready-mix truck. Before the placement, a representative tailings sample is collected to determine its slump and water content for each layer. The slump varied between 200 mm and 290 mm while the corresponding water content was between 29% and 33.4%. Results are listed in Table 2.

Table 2. Summary of initial water content and slump values of paste tailings

	-	-	_	
Layer	Initial water content		Slump va	lue
no	CC wt%	UC wt%	CC mm	UC mm
1	32.8	32.8	240	240
2	31.9	29.0	230	230
3	29.4	29.4	240	220
4	31.8	31.8	220	230
5	32.0	32.4	230	240
6	29.9	29.8	240	240
7	33.4	33.0	250	240
8	32.8	33.4	240	250
9	33.3	38.2	250	290
10	33.2	33.3	250	250

Tailings disposal configurations refer to the layering patterns of the different layers of paste materials with or without cement. The deposition frequency was set at one layer every 1 to 3 weeks, based on the paste plant schedule and the tailings availability. Figure 7 shows a schematic view of experimental cells designed. The corresponding photos are shown in Figure 8.

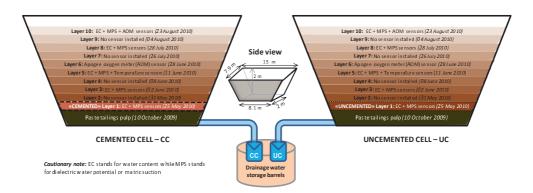


Figure 7. Schematic view of the field cells installed in two different configurations



Figure 8. Photos illustrating a fresh paste tailings layer placement

Each stack deposited (cemented or uncemented) was made up of 10 paste layers, each having a thickness of approximately 10 cm to mimic full scale field SPD. The main reason behind this thin layer deposition application is to let the paste material gain faster strength through desiccation because thick layers do not permit enough desiccation to stop flows as the stack rises in height. The first layer of the cell is cemented to show the

cementation effect as a capillary barrier layer on mitigation or prevention of acid mine drainage. The binding agent used was 100 wt% normal Portland cement at a binder content of 2 wt% alone. After deposition of each layer, the deposited angle of the layer is monitored and adjusted to make sure that ground surface is flat. Between each layer deposition, photos are taken to typify the phenomenon of desiccation.

2.2.3 Sensor Installation and Monitoring

To monitor climatic conditions such as wind, temperature, rainfall, and humidity, a station was installed on testing area. A total of five water content sensors, five suction sensors, two oxygen consumption sensors, and one temperature sensors were used for two cells. The Decagon[®] EC-5 water content probes are calibrated with tailings (with and without cement) before installation (Figures 9a, 9b). The EC-TM moisture/temperature sensors (Figure 9c) were besides calibrated for only Layer 5, which contains uncemented tailings.

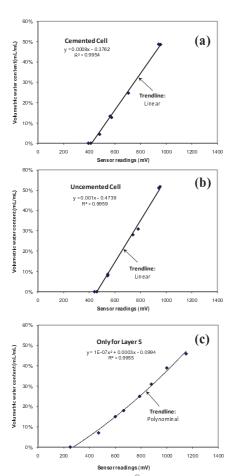


Figure 9. The Decagon[®] EC-5 and EC-TM Esensor calibration curves for cemented (a), uncemented (b), and uncemented layer 5 (c) configurations, giving a coefficient of correlation close to 1.

3 RESULTS AND DISCUSSION

3.1 Volumetric Water Content Evolution

Figure 10 shows the evolution of the VWC measured by ECH₂O EC-5 sensor located in Layers 1, 3, 5, 8 and 10 for uncemented and cemented paste tailings. The general trend of the VWC curves is that it decreases radically during the first 3-4 hours following by paste deposition, later remains constant for a long time, and again starts to decrease. This is mainly due to the effects of evaporation and removal of excess water by self-weight consolidation settlement.

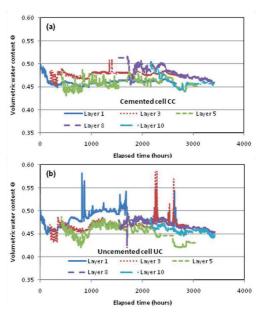


Figure 10. Variation in VWC with time for paste tailings in CC and UC configurations

VWC varied between 0.45 and 0.5 for each depositional condition. Due to the fact that Layer 1 of paste tailings in the CC is made by a proportion of 2 wt% of cement, it acts differently because of paste's microstructure changes by the possible dissolution of cement compound and keeps more free waters in its structure than the rest of layers, including the UC (Figure 10a). In this case, the VWC in Layer 3, 5, 8 and 10 relatively increases because of re-saturation by free

water drained after the layer of paste placed is fully settled. The part of water flowed through desiccation crack network reaches and stay in cemented (2 wt%) layer, which acts as a barrier cover. That's why the lowest VWC are recorded by Layer 1, unlike other layers. However, in case of UC, the highest VWC value is recorded in the bottom layer (Layer 1) due to water accumulation drained from Layers 3, 5, 8 and 10 (Figure 10b).

3.2 Matric Suction Evolution

Figure 11 shows the variation of suction ψ of both cemented and uncemented tailings as a function of elapsed time since the deposition of Layers 1, 3, 5, 8, and 10, respectively. The data was recorded at a time interval of 5 minutes. It can be observed that the matric suction increases with the coupled effects of de-saturation by a new paste layer placement and therefore infiltration. The maximum suction increases of about 42 kPa for Layer 3 and of about 52 kPa for Layer 10 (Figure 11a) were observed from cemented cell. The maximum suction was recorded from Layers 3 and 5 in UC (Figure 11b).

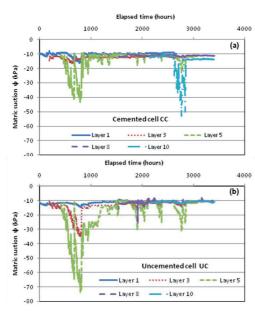


Figure 11. Variation in suction with time for paste tailings in CC and UC configurations

3.3 Degree of Saturation Evolution

Figure 12 presents the variation in degree of saturation of paste tailings in the CC and UC with time. In this study, the S_r is calculated from the VWC divided by its corresponding in-situ porosity taken after gravity driven consolidation settlement of paste layers. It should be stated that although the in situ porosity tests give a significant contribution to determine the S_r parameter, it does not consider surcharge consolidation settlement happened by the placement of the new paste layers. This phenomenon is kept in mind while interpreting the results.

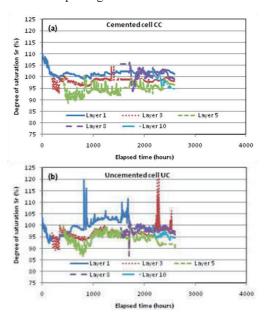


Figure 12. Variation in degree of saturation with time for paste tailings in CC and UC configurations

As expected, the bottom layers, especially for Layers 1 and 3) are more saturated (closely to 100%) than the top layers due to the consolidation settlements which reduce void spaces among solid particles. For fine-grained tailings, thinly-placed layers provide a faster settlement than thickly-placed layers. The S_r of paste tailings varies between 87% and 110% and reaches a plateau following a slight increase after deposition is completed.

Layers 1, 3 and 5 respectively result in the constant S_r value of 100%, 98%, 95% for the CC, and of 99%, 96%, and 94% for the UC. Due to the fact that the first layer is consisted of cement (2wt% of Portland cement) in the CC (Figure 12a), and acts as a barrier cover, the layers in this cell keeps more water in the matrix than the ones of the UC condition, resulting in higher saturation. The S_r curves demonstrate similar behavior of evolution over the time, except for the first layer in the UC. The S_r increases slightly and reaches the highest value at a storage time of 1500 hours that corresponds to Layer 7. Then, it remains constant (generally 100%) at the remaining paste layers. This confirms that the paste needs to retain water to get its maximum saturation up to Layer 7 and then remains fully saturated by the coupled effects of gravity-driven and time-dependent surcharge consolidation loadings.

3.4 Top Surface Crack Measurement

Figure 13 shows photos of top surface cracks (Layers 1 and 10) of deposited paste tailings

in the CC and UC configurations. One can observe clearly that, irrespective of the layer, the first five layers shows more cracks than the remaining five layers due to climatic condition where evaporation is higher than precipitation for the deposition time. On the whole, the width, length and depth of cracks that occurred in UC are relatively larger than the ones in CC. This may be well explained either by continuous water consumption or retention (increased saturation) of cemented layer by freshly-placed paste addition and self-desiccation processes.

One can also interpret by the total number of cracks that decreases with the increasing number of deposited paste layers, but the width and depth of these cracks get larger since they seem to re-open in previously-occurred cracks at similar locations in the cells. Researchers (Benzaazoua et al., 2004; Simms et al., 2007) have showed clearly that most of the cracks occurred right after the layer deposition are mainly a result of the desiccation process and are closely related to the shear strength gain of tailings.

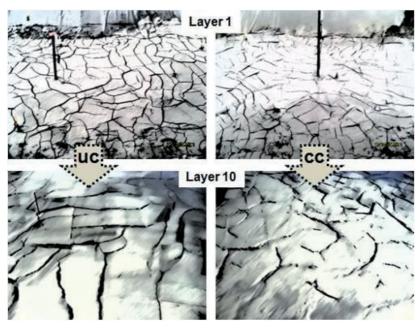


Figure 13. Surface cracks in layers 1 and 10 for UC and CC configurations.

Table 3.	Range of	crack	width.	length	and de	nth of	paste tailings

Layer	Range of crack width		Range of o	Range of crack length		Range of crack depth	
no	CC – mm	UC – mm	CC – mm	UC – mm	CC – mm	UC – mm	
1	17-20	20-23	56–65	56-67	56–68	57-71	
2	10-12	21-24	45-51	65-78	42-51	58-64	
3	12-16	13-16	46-59	65–75	48-53	73-80	
4	10-12	16-18	63-65	74-88	62-70	64–68	
5	10-11	14-18	72-77	78-88	46-54	76-82	
6	13-16	16-19	64-80	83-86	61-72	76-82	
7	13-16	16-18	77–85	80-97	70-80	26-37	
8	12-16	18-21	68-82	78–87	25-31	38-46	
9	15-17	17-20	74-83	91–96	34-44	80-88	
10	14-16	18-22	79–85	92–95	65-72	76–85	

Note 1: CC stands for cemented cell while UC stands for uncemented cell

Note 2: Results are based on the average value obtained from 5 tests for a given cell

Table 3 lists a range of top surface cracks in terms of width, length and depth for paste tailings in the CC and UC configurations. The crack width reduces or the crack depth increases as the number of layers increases. The range of the crack width is reduced from 17-20 mm to 14-16 mm for the CC, and is reduced from 20-23 mm to 18-22 mm for the UC, while the crack depth is increased from 56-58 mm to 65-72 mm, and from 57-71 mm to 76-85 mm for CC and UC configurations, respectively.

Note that the formation of top surface cracks is dependent on the time interval and configuration of the deposition. The longer the deposition process is, the deeper and wider the cracks are. The drainage of upper layer is accelerated after the deposition of freshly-placed tailings on a dry surface layer. This is due to the suction developed by the layer below, which creates a fast movement of water towards the bottom and might lead to a fast crack occurrence. This phenomenon is well observed in the first layers.

3.5 Geochemical Behavior of Leachate

Figure 14 presents the results of chemical analysis of leachate waters collected from the bottom of each cell after the deposition of paste tailings in comparison with tailings interstitial pore water. One can observe that Ca, Fe, Mg, Mn, Si and Zn are high in collected water in comparison to control samples (pore water) and tend to diminish

over time. No leachate water is collected from the first three layers in the CC and UC due to no water accumulation on the surfaces of the cells. It is also observed that there is no colour change in all the collected leachate waters up to now, which well indicates paste tailings have not oxidized even though there occurs numerous cracks on the surface right after their placement. As well-known, the cracks developed on surface can change the distribution of water and oxygen in the cells, and affect the tailings oxidation, producing acid and toxic metals. The concentration of As, Cu, Fe, Ni, Pb and Zn in waters released from the cells is ower than the allowed values of 0.2 mg/L, 0.3 mg/L, 3 mg/L, 0.5, 0.2 mg/L, and 0.5 mg/L, respectively, as determined by Directive 019 on mining industrial wastes in Quebec, Canada.

Figure 15 shows the variation in sulphate SO₄², pH, oxidation-reduction potential Eh, and electrical conductivity EC of collected leachate water with time for each cell, comparing them to control sample. One can say Eh (increases from 175 mV to 355 mV) of leachate waters is higher than control samples while pH (varies between 6.8 and 8) and EC (decreases from 6.4 mS/cm to 4.5 mS/cm) are lower than control samples, mainly due to the release of heavy metals from tailings. The oxidation of sulphide-rich minerals (e.g., pyrite FeS₂) in tailings leads to a decrease in pH of the solution. However if cemented tailings is used, then the pH increases because of an alkaline medium.

The Eh is related to the acidic and basic solutions as well as degree of saturation S_r . When Eh is positive, the solution contains oxidizing compounds. Eh increases with the decreases of S_r which contributes to the

increase of oxidation by molecular oxygen diffusing through the leachate water samples. The Eh increases slightly, resulting in a release of free ions within the solution (e.g., calcium and sulphate).

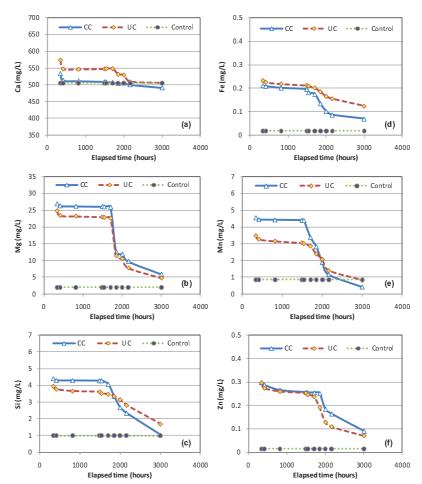


Figure 14. Variation in Ca (a), Mg (b), Si (c), Fe (d), Mn (e), and Zn (f) of collected leachate waters with time

Eh-pH diagrams, called Porbaix diagrams, are also useful tools to better visualize the stability areas of metal species in a solution depending on the solution's redox potential Eh and pH. In the diagram the dotted red lines represent the stability area of water, i.e. the area of relevance for hydrometallurgy. The upper line is the equilibrium between

water and oxygen gas. If the solution potential is increased above the dotted red line, water is oxidized forming oxygen and hydrogen ions. The lower line shows where hydrogen ions in a solution are reduced to hydrogen gas. Figure 16 shows the Eh-pH diagram of leachate collected, considering control sample (tailings pore water).

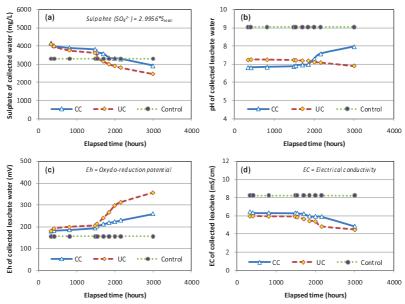


Figure 15. Variation in sulphate (a), pH (b), Eh (c), and EC (d) of collected leachate waters with time

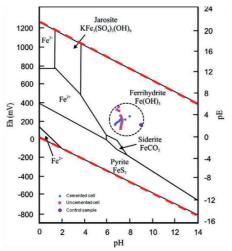


Figure 16. The Eh-pH diagram of leachates

One can interpret that the leachate waters collected exhibit an oxidizing and alkaline medium which favour the precipitation of iron in iron hydroxide Fe(OH)₃. This also shows that at this high pH range, a major lag time occurs before the tailings oxidation and hence acidic seepage is generated.

4 CONCLUSIONS

A field experimental study that consists of two cells (cemented cell CC and uncemented cell UC) was carried out at the LaRonde Mine (Quebec, Canada) to better investigate a possible application for surface disposal of fine-grained, sulphide-rich paste tailings. A multilayer deposition configuration (10 layers of about 10 cm thick) is considered for assessing the reliability and workability of the field cells by running some preliminary tests. Sulphide-rich tailings are prepared in the paste plant, transported by a read-mix truck to the construction mine site, and then deposited in the cells layer by layer. All the layers were made of uncemented tailings, except layer 1 in the CC where 2 wt% of cement is added to the tailings. This cement addition was chosen to evaluate the leachate reduction potential by the release of heavy metals and to prevent the tailings oxidation by making layer saturated, thus eliminating the diffusion of oxygen.

Based on the preliminary results of the present field experimental cell study, the following conclusions can be drawn:

- ➤ The VWC varied between 0.42 and 0.52 and decreased slightly during the first 3-4 hours after the deposition, later reached a plateau for a long time, and finally started to re-decrease. This is due to consolidation settlement and removal of excess water from tailings.
- > The suction of tailings in CC is lower than the one gained by UC because of water retention by layer accumulation and formation of top surface cracks by evaporation. The more cracks form, the more the suction within tailings develops at a given temperature.
- ➤ Surface crack measurements show that the width, length and depth of cracks increase with the increasing number of accumulated layers. This behaviour is due to the reappearance of alreadyoccurred cracks in prior layers by the effects of evaporation and settlement.

Although this cell testing provided key information regarding the surface disposal of paste tailings as a viable disposal alternative, further works are required to better identify the hydro-geotechnical behaviour of paste. These further steps are as follows:

- ➤ Coring samples are required to assess the microstructural properties of each paste layer.
- Long-term geochemical monitoring of leachate water collected from each cell is required to observe the efficiency of the cemented layer acting as capillary barrier cover.
- Analysis of the crack intensity factor should be made to determine some relationships between water content, suction, temperature, and desiccation cracks occurring in paste tailings.

All of the above-mentioned aspects are presently underway for understanding the SPD's in situ behaviour. It is believed that the results of these works will bring a new light to waste planners and operators and modern mines will shift their current tailings management systems to paste technology.

ACKNOWLEDGEMENT

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Pre-selection Methodology for the EU Mine Waste Directive Inventory of mine waste sites to support risk assessment in a European Union context. Case studies from EU Member States and Turkey

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ABSTRACT The EU Mine Waste Directive (MWD) requires the risk-based inventory of all mine waste sites in Europe by 2012. Major incidents involving mine waste facilities in the historic mining areas in the Carpathian Basin and the associated environmental risks have triggered the development of new EU environmental legislation to prevent and minimize the effects of such incidents. In order to address the mining environmental problems a standard risk-based pre-selection protocol has been developed by the EU Commission. This paper evaluates the protocol by applying it to real-life cases and carrying out uncertainty analysis. All together 145 ore mine waste sites have been selected for scientific testing and evaluation using the EU Pre-selection Protocol as a case study from Hungary. Key parameters such as the topographic slope and distance to the nearest surface and groundwater bodies, to settlements and protected areas are calculated and statistically evaluated in order to calibrate the risk assessment models to local conditions. According to the results, out of the 145 sites, 11 waste sites are the most risky with topographic slope >200, 57 sites are within distance less than 500m to the nearest surface water bodies (streams and lakes), and 33 sites are within distance less than 680m to the nearest settlements. Moreover, 25 sites are located directly above the groundwater bodies with 'poor status' and 91 sites are located inside the protected Natura 2000 areas. According to the number of YES responses of the Pre-selection Protocol, a relative risk-based site ranking was performed using STATGRAPHICS® statistical software which resulted in 127 sites are directed to 'Examine Further' using EU thresholds and 129 sites directed to 'Examine Further' using local median-based thresholds. In addition to, 16 sites without pathway (based on EU thresholds) and 18 sites (based on the local thresholds) are directed to 'No Need to Examine Further'. Similar study is being carried out in Turkey with EU support under the accession process to provide inventory of the Turkish mine waste sites.

1 INTROUCTION

Mining, milling operations and abandoned mines are a significant problem in areas with long historic mining like Europe, because mine closure practices have changed with

time and environmental protection has not been considered for closed mines until recently (Jordan 2004; Navarro et al. 2008). Apart from that abandoned mines are the same as active mines in terms of types of

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hazard and potential impact on the environment; their major problems are uncertainty in information and lack of control. Direct exposure to the acid mine drainage (AMD) and sediments discharged from abandoned metal mines poses a serious hazard to aquatic biota and to humans (Panagopoulos et al. 2009; Sarmiento et al. 2011). There are an estimated 3 million potentially contaminated sites in the whole European Union, of which about 250,000 are actually contaminated and in need of remediation (EEA, 2007).

Significance of contamination risk posed by mining is highlighted by mine accidents (Jordan and D'Alessandro 2004). Examples of such accidents which classified as an engineering risk are 1) Wales, UK, in 1966, Stava, Italy, in 1985, Aznalcollar, Spain, in 1998, Baia Mare, Romania, in 2000. Most recently, an estimated 0.9-1 million cubic meters of alkaline (pH >13) caustic red mud spilled through the failed dam of the Ajka alumina plant depository on October 4, 2010 in Kolontar, Hungary, resulting in loss of lives and contamination of agricultural land (Jordan et al. 2011).

1.1 Directive 2006/21/EC (Article 20) — risk-based inventory of abandoned mine waste sites

The EU Directive on the Management of Waste from the Extractive Industries 2006/21/EC, Waste (Directive Mine Directive (MWD)) requires in Article 20 that Member States shall ensure that an inventory closed waste facilities, including should abandoned waste facilities accomplished by 2012 using risk assessment (RA) methods. According to Article 21, such methods shall allow for the establishment of the most appropriate risk assessment procedures and remedial actions in Europe.

1.2 Risk assessment (RA)

Contamination Risk assessment (RA) is defined as the probability of adverse effects to humans and ecosystem resulting from exposure to environmental pollutants (CARACAS 1999; US EPA 1989; 1998), therefore RA is concerned with the risk involved at a specific site, at a specific time, and due to specific causes. RA includes the steps of 1) hazard description, analysis, 3) dose/response (toxicity) contaminant transport, 4) exposure assessment, 5) risk characterization, and 6) risk management (Van Leuwen and Hermens 1996; U.S. EPA 2002; 2007). Contamination risk exists for a site only if all the source, pathway and receptor components are present. In the case of mine waste sites, for example, this means that a hazardous waste should be present such as an ore tailings pond, contamination transport should be enabled by air, surface- and groundwater or direct contact to reach sensitive receptors such as settlements, protected ecosystems or agricultural lands. Regional RA is a quantitative methodology to estimate and compare the impacts of environmental problems that affect large geographic areas (Landis, 2005) and/or multiple contaminated sites (Pizzol et al. 2011). Mine site characterization and risk-based ranking methods have been reviewed and evaluated by national and international efforts (Horvath and Gruiz 1996; Sommer et al. 2003; Rapant et al. 2006; Bagur et al. 2009; deLemos et al. 2009; Broadhurst and Petrie 2010; Pizzol et al. 2011; Moreno-Jiménez et al. 2011; Turner et al. 2011; Yenilmez et al. 2011). U.S. EPA (2001) gives detailed description of riskbased assessment of mine sites. Moreover, as for the prioritization process, the Soil Thematic Strategy for soil protection (COM (2006) 231) and the EU MWD (Directive 2006/21/EC) point out the need to develop risk-based methodologies sustainable management of contaminated sites and mining waste sites at regional scale. The effort required to identify and prioritize contaminated sites in Europe is considerable (EEA 2005).

The objective of this paper is to evaluate the EU MWD Pre-selection Protocol (Stanley et al. 2011) by applying it to real-life cases from Hungary as an EU Member State and to carry out uncertainty analysis. It is not the objective to report on the national inventory by any means; in fact, the site data used here for scientific development are not based on the reported inventory data. A detailed statistical analysis is carried out for the measured distances to pathways or sensitive receptors, topographic slope and census data and the new values developed are adapted to the local conditions in Hungary. This also enables the evaluation of the Protocol in terms of sensitivity to various thresholds. Moreover, a simple uncertainty analysis is carried out, and the Protocol is evaluated against the number of uncertain responses to the questions on the 18 key parameters involved.

2 METHODS

2.1 Principles and characteristics of the protocol

The EU MWD Pre-selection Protocol (Stanley et al. 2011) is based on a 'YES-or-NO' questionnaire (Fig. 1) and consists of 18 questions using simple criteria available in existing databases readily enabling the preliminary screening of the mine waste sites for environmental risk. This screening should result in the elimination of those sites which do not cause or have the potential to cause a serious threat to human health and the environment from the inventory of closed waste sites. Note that even if a waste facility passes the pre-selection protocol and classified as EXAMINE FURTHER, it does not mean that the closed waste facility will necessarily be included in the final inventory. For example, the Mád waste site in Hungary passed the protocol with 6 YES responses to the questionnaire questions (4 questions in the source and 2 questions in the receptor sections) and 9 NO responses and it was classified for EXAMINE FURTHER. But there is no pathway existing in this site by which receptors could be impacted by the toxic mine waste source, therefore the site will not be included in the final inventory. In Annex III of the MWD criteria for determining the classification of waste facilities, indents 2 and 3 specifically refer to hazardous and dangerous substances being above a certain threshold. These thresholds have been fixed by Commission Decision 2009/337/EC. Since the pre-selection protocol is meant not to involve field sampling or laboratory analysis, any level will be sufficient to pass the test and select the site for further investigation as a precautionary measure.

Based on Article 20, the pre-selection protocol should possess the following characteristics: 1) be risked-based, i.e. consider both the probability of an event occurring and the impact of such an occurrence, 2) address the source, pathway and receptor paradigm, 3) be simple and office-based, 4) use readily available data, 5) address data and information uncertainty, 6) address serious damage to both human health and the environment (ecosystem) receptors, 7) assess whether the closed waste site contains either hazardous waste or dangerous substances, 8) assess the physical stability of the closed waste site, 9) address serious damage occurring at the present and the potential for such damage to occur into the future (medium term, i.e. 1 to 10 years), 10) provide a selection of waste sites for further assessment, 11) produce a selection of waste facilities that would be reasonably certain of capturing all relevant facilities, precautionary, 12) be reasonable proportionate for the task.

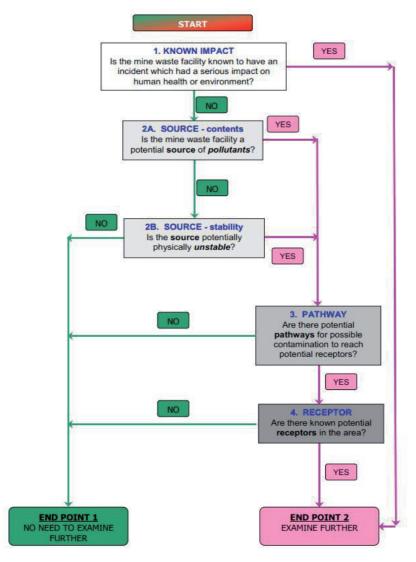


Figure 1. The EU MWD Pre-selection Protocol Flowchart

2.2 Parameters and thresholds

The EU MWD Key parameters, such as the distance from a mine waste site to the nearest receptor (settlement, protected area, etc.) and the topographic slope under the waste site are used in this Pre-selection Protocol, in order

to identify those sites that might cause serious environmental impacts. The EU thresholds (1km distance and 50 in slope) are based on the Irish regulations for the operation of ponds with respect to quarries (Safe Guard, 2008). In this study, the median values of topographic slope and distance to the nearest surface water course (Q11), settlement (Q15), groundwater bodies (Q16), Natura 2000 sites (Q17) and to agricultural areas (Q18) are used as local thresholds

(Median-based) adapted to Hungarian conditions. Therefore, each Member State can choose a different threshold which can meet their particular circumstances or experience.

3 MATERIALS

Two types of available data are used in this study as follow:

- 1. Basic waste site data: a) location of waste sites as points (polygon centroids) (Fig. 2), b) contents of waste sites including sulphides, toxic metals, and dangerous substances, c) information on chemicals used during mineral processing, d) information on the geometry of the waste heap (volume, area, height), and slope of foundation, e) other data such as presence of high permeable layer beneath the waste site, and if the facility is exposed to wind or if it is uncovered (Q13, 14).
- 2. Basic spatial and census data: a) topographic data including location of human settlements as polygons, surface water courses (streams and lakes) (Fig. 2), and slope data calculated for each waste site from the Hungarian national contour based 50m DEM using ILWIS® 3.7 open source software (Fig. 3), b) census data (2009) is available from the Hungarian Central Statistical Office (www.ksh.hu), c) data on the national protected areas (Natura 2000 sites) (Fig. 1) available from the Hungarian Central Directorate of Water Environment (http://www.vkki.hu), location, status classification, monitoring data of groundwater bodies in Hungary under the Water Framework Directive and available http://www.eea.europa.eu/dataandmaps/data/waterbase-groundwater-7, Land use/land cover data (LULC) maps at 1:100,000 scale are available in Europe from

(http://www.eea.europa.eu/publications/COR 0-landcover).

All together 145 ore mine waste sites (Fig. 2) are tested using the EU MWD Preselection Protocol as a case study from Hungary. Then by running the protocol, the number of YES, NO and UNKNOWN responses are registered for each site. The proportion of the certain to uncertain responses for a site and for the total number of sites may give an insight of specific and overall uncertainty in the data we use (Table 1). The distance from mine waste sites to the nearest stream (Q11) and receptors (Q15-Q18) is measured using proximity analysis tools (Generate Near Tool) in ArcINFO® 10 (Fig. 2). In order to identify if there is a high permeable layer beneath the mine waste site (Q12), a surface permeability map for the geological formations of the 1:100,000 surface geological map of Hungary has been constructed using ArcINFO® 10 on the basis of the geological characteristics of the uppermost rock units considering the estimated hydraulic conductivity, porosity, permeability values of rock units used in hydraulic models. Three groups have been distinguished. Group of formations with lowpermeability (clay and other impermeable formations). with medium-permeability sand-gravel and fractured metamorphic and volcanic rocks) and with high-permeability (karstified limestones and dolomites belong to this group). Polygons of the mine waste sites derived from the CORINE land cover 1:50,000 maps (CLC 2000) are overlaid by Google Earth® aerial photographs (2010-2011), in order to identify if the material within the mine waste sites is exposed to wind or not (O13) or covered or not (O14), since the air and direct contact pathways are related to the aerial exposure of mine waste heaps. Local threshold values are based on the natural breaks in frequency histograms and in the cumulative distribution functions of the key parameters using Centurion XV.II® **STATGRAPHICS** software.

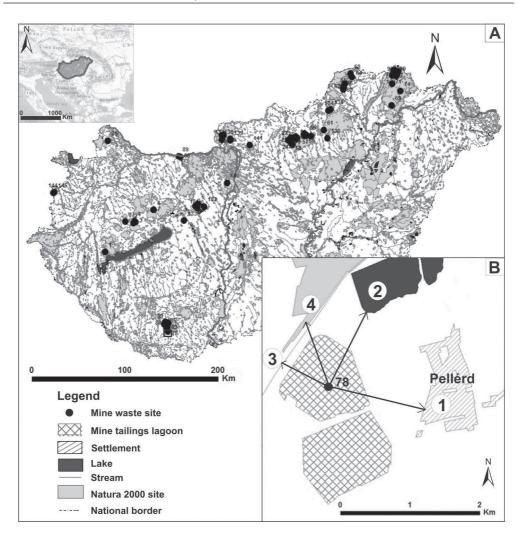


Figure 2. A. Mine waste sites in Hungary in this study. Solid box shows location of Figure 2B. B. Distance measurement from the waste sites (polygon centroid) to the nearest settlement (1), surface water lake (2), stream (3) and to the nearest Natura 2000 protected area (4).

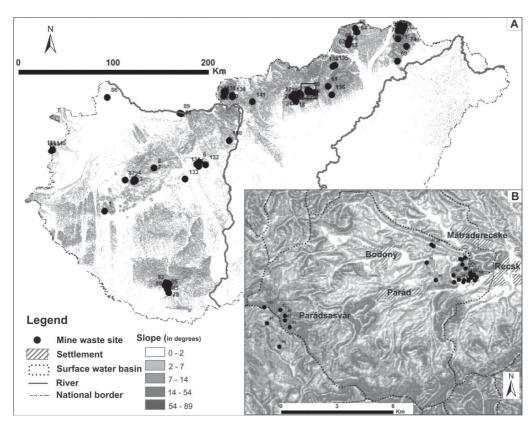


Figure 3. Topographic slope map for Hungary. A. Using the national contourbased 50m grid DEM. Solid box shows location of Figure 3B. B. An example for the Recsk Mining Area, the Parád Tarna Creek catchment.

4 RESULTS AND DISCUSSION

4.1 Using EU thresholds

The EU MWD Pre-selection Protocol (Stanley et al. 2011) The YES, NO and Unknown (U) responses of the EU MWD Pre-selection Protocol (Fig. 1) using EU thresholds (slope of 50 and 1km distance from waste site to receptor) are registered and calculated for each question in Table 1. Out of 145 mine waste sites, only 19 sites

have had a documented incident (Q1) such as the collapsed dam of the Ajka alumina depository in Kolontár, Hungary, in 2010. These 19 sites are immediately redirected for further examination in the EU MWD Preselection Protocol. For question 2 (Q2), 101 sites with YES responses were producing waste with sulphide minerals, 40 sites have NO responses, and the other 4 sites (3% of studied sites) with UNKNOWN responses. While 126 sites with YES responses were producing minerals with toxic heavy metals, 15 sites have NO responses, and 4 sites (3% of the total number of sites) have UNKNOWN responses (Q3). Seven sites with YES responses have documented use of dangerous chemicals for the mineral processing, 138 sites have NO responses (Q4). In Q5, 9 sites are tailings lagoon sites and 136 sites are waste heaps.

The area of each of the 9 tailings lagoons is greater than the 10,000 m2 threshold in Q6. Only 4 tailings lagoons with YES responses are >4m in height within 50m of the waste site, while two sites with NO responses are <4m and the other three sites (33% of the 9 tailings lagoons) have UNKNOWN responses (Q7). In Q8, 34 waste heap sites with YES responses are greater than 10,000 m2 in surface area and 10 waste heaps aerial extent (7% of the 136 waste heaps) is unknown. In Q9, 9 waste heap sites are >20m height and 12 sites (9%) have UNKNOWN heights. The slope of the foundation upon which the waste heap rests is of concern with respect to stability. The greater the slope angle the greater the risk of the waste heap failing. In Q10 the topographic slope (in degrees) is defined from the Hungarian national contour based 50m DEM for each waste site (Fig. 2). The EU threshold chosen is 1:12 which equates to 8.3% or a slope angle almost 5°. 110 waste heap sites with YES responses are greater than or equal 1:12 (50) in slope and 26 sites with NO responses are less than 50 (Q10). For Q12, 120 sites with YES responses (three sites underlain by High permeable layers and 117 sites underlain by Medium permeable layers), while 25 sites underlain by Low permeable layers. In Q13, 17 sites are exposed to the wind and 128 sites are not. While 17 sites are uncovered and 128 sites are may be covered with water, vegetation, soil and forests (Q14). For Q11, 64 sites are within 1km distance to surface water bodies (streams and lakes). In Q15, 45 mine waste sites are within 1km distance to nearest human settlements with >100 people. In Q16, 28 sites are within 1km distance to the groundwater bodies of less than good status (poor status). For O17, 131 mine waste sites are within 1km to the national protected 'Natura 2000' sites (91 waste sites are completely inside the protected Natura 2000 sites), and 14 sites are within distance >1km.

Moreover, 84 sites are within 1km distance to the agricultural areas including arable lands, pastures, heterogeneous and permanent crops (Q18).

4.2 Using local (median-based) thresholds

distribution analysis Statistical performed for slope (Q10) and the nearest distance to the pathways and receptors (Q11, Q15-18) in order to develop new risk thresholds to be adapted to Hungary. The local thresholds (median-based) that derived from the median values of slope and distance data are the following: 10° for the slope below the waste site (Q10), 760 m for the distance to surface water bodies (Q11), 1,722 m for the distance to settlements with almost 820 inhabitants (median-based) (Q15), 6,044 m for the distance to groundwater bodies with 'poor status' (Q16), 470 m for the distance to highly protected Natura 2000 sites (Q17) and 612 m for the distance to the agricultural areas (O18). In order to develop a population threshold value for Q15, a distribution analysis was performed on the most recent population census data of Hungary resulting in 53 classes ranging from <45 to >45.000 persons. The analysis indicates that 1,670 settlements with less or equal to 820 persons are representing 53% of the total number of settlements in Hungary. Therefore the figure 820 is chosen as a local threshold (median-based) for the population in Q15. By running the EU MWD Preselection Protocol using these local (medianbased) thresholds, the YES, NO and Unknown responses are registered for each site and compared to those of EU thresholds (Table 1). Table 1 shows that the number of waste sites with YES is different from those using the EU thresholds to local thresholds for each question. For example, in Q10 for slope, sites with YES responses are decreased from 110 (EU thresholds) to 74 (local median-based thresholds). This shows that mining sites mostly found in hilly areas

are located on steeper slopes in Hungary than mining sites in Ireland, where the EU thresholds were adapted from. For Q11 on the distance to nearest water course, the sites with YES responses are increased from 64 (EU thresholds) to 73 (local median-based thresholds). This is explained by the fact that mines are located in the steep valleys of the hilly areas in Hungary rendering the horizontal distance to stream (valley bottom drainage line) short.

Uncertainty is inescapable in assessment of environmental hazard. exposure and the consequent risks to human health, and it arises at every stage in these assessments (Ramesy 2009). It causes an increased risk of incorrect decisions being made in the assessment, particularly if the uncertainty is ignored in a deterministic approach, or just underestimated in a probabilistic approach. In this uncertainty is limited to the unknown responses (U) in each question of the EU MWD Pre-selection Protocol due to the lack of specific data about the mine waste sites. Table 1 indicates that Uncertainty (U) is concentrated in the source questions, ranging from 3% in Q2 and Q3 (source contents, sulphide minerals) and 7% in Q8 (source stability, 10,000 m2 area of the waste heap) to 33% in Q7 (height of the mine tailings lagoon). Therefore, if the source questions are empirically relax, the percentage of uncertain responses (U%) will be reduced to Moreover, most of the digital topographic maps used in this study have 1:100,000 scale, therefore uncertainty in distance measurements in O11, O15-18 is estimated as more or less as 100 m.

A risk-based site ranking system based on both EU and (local median-based) thresholds, is carried out by counting the YES responses of the EU MWD Preselection Protocol for the source, pathway and receptor sections in each waste site. 127 mine waste sites are directed to EXAMINE

FURTHER based on the EU thresholds, and 18 sites with no risk (without pathway). 129 sites are directed to EXAMINE FURTHER based on the local (median-based) thresholds, while 16 sites without pathway.

5 CONCLUSIONS

The EU MWD Pre-selection Protocol provides a systematic methodology for the pre-screening and ranking of contamination risk associated with the mine waste sites. This RA is based on a fundamental understanding of the key factors and parameters controlling the contamination fate along the source-pathway-receptor chain and the chemical behavior of wastes in the mine sites. Besides forming a necessary part of efficient risk-based contamination assessment of large number of mine waste sites, the pre-screening RA achieved by the EU MWD Pre-selection Protocol outlined and tested in this study plays a key role in the first stage decision-making.

Similar study is being carried out in Turkey with EU support under the accession process to provide inventory of the Turkish mine waste sites.

Table 1. Summary statistics of the EU MWD Pre-selection Protocol responses of questions Q1-18, showing the number of YES and NO responses based on the EU Pre-selection Protocol thresholds, and the local median-based thresholds. The number (U) and percentage of certain to uncertain (U%) responses for each question, based on the number of UNKNOWN responses. Bold indicates questions and statistics depending on threshold values.

Pre-selection Protocol		Number of Sites	thresl	EU holds	thresl	edian-	1	U %
Impact	Q1	145	19	126	19	126	(0
	Q2	145	101	40	101	40	2	3
	Q3	145	126	15	126	15	2	3
	Q4	145	7	138	7	138	(0
	Q5	145	9	136	9	136	(0
çe	Q6	9	9	0	9	0	(0
Source	Q7	9	4	2	4	2	1	3
	Q8	136	34	92	34	92	0	7
	Q9	136	9	115	9	115	2	9
	Q10	136	110	26	74	62	(0
ž	Q11	145	64	81	73	72	(0
Pathway	Q12	145	120	25	120	25	(0
att	Q13	145	17	128	17	128	(0
Ь	Q14	145	17	128	17	128	(0
or or	Q15	145	45	100	73	72	(0
l dd	Q16	145	28	117	73	72	(0
Receptor	Q17	145	131	14	112	33	(0
×	Q18	145	84	61	73	72	(0

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Laboratory and In Situ Analysis of Consolidation Behaviour of Cemented Paste Backfill

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ABSTRACT This paper aims at examining the consolidation behaviour and time-dependant strength gain of the cemented paste backfills (CPB) made using different binders. Two types of consolidation tests were realized: lab-scale tests via a tool named CUAPS (curing under applied pressure system); and field-scale tests via three columns installed at a paste plant. From the physical tests, one can say that, for a given binder amount, the void ratio, degree of saturation of drained CPBs are pretty lower than those of non-drained ones. The maximum observed consolidation settlement occurs within the first 72 hours since columns are filled. At last, this study shown that CUAPS and columns could be used as valuable tools to collect reliable data and to assess some conditions on CPB performance in lab and field tests.

1 INTRODUCTION

Cemented paste backfill (CPB) is used on a wide scale in today's underground mining sector. CPB offers environmental benefits by minimising large surface waste dams and safety benefits by reaching higher strengths with equal cement consumption as compared to other forms of backfill such as hydraulic and rock backfills (Potvin et al., 2005; Belem and Benzaazoua, 2007; Yilmaz, 2011). CPB is mainly prepared by mine tailings which are mixed with water and binder. Significant progress has been so far made in realizing the quality of lab-made CPB by focussing on its material properties (Benzaazoua et al., 1999, 2004; Kesimal et al., 2005; Belem et al., 2006; Ercikdi et al., 2009; Fall et al., 2009, 2010; Yilmaz et al., 2011a; 2013, Cihangir et al., 2012), but little effort is made to study in situ performance and quality of CPB (Hassani et al., 1998; Cayouette, 2003, Belem et al., 2004; le Roux et al., 2005; Thompson et al., 2011, 2012). It is observed from Canadian mines that the strength of the in situ CPB cores was up to 6 times higher

than that of lab-made ones using the same recipe and curing ages. The reasons behind this observation is due to the mechanisms of fresh or hardened CPBs within the stope during curing (i.e., enhanced consolidation and scale effect) and bleeding occurred by the settlement of solids with the expulsion of water (i.e., the paste's stiffness, Fourie et al., 2007; Helinski et al., 2007, 2011; Yilmaz et al., 2009; Yilmaz, 2010; Fahey et al., 2011). In general, these circumstances happened in underground are more often ignored in many studies seemingly due to the unavailability of an appropriate lab system for studying the consolidation and drainage conditions.

Measuring the in situ material properties is of a great importance in optimizing a CPB mix design in terms of strength, stability and cost saving (Fall et al., 2008; Benzaazoua et al., 2008; Belem et al., 2010; Yilmaz et al., 2011b). These properties of CPB can be also simulated at laboratory via one-dimensional consolidation tests by applying a number of stress increments to paste samples (Belem et al., 2002; Yilmaz et al., 2008, 2010, 2012;

Fahey et al., 2011; Helinski et al., 2011). A number of different in situ conditions can be also considered in lab-made CPBs by using bottom-perforated plastic moulds to allow drainage of water during curing. A relatively few experimental studies are reported in the literature on the self-weight or gravity driven consolidation of waste rock and mill tailings (Wickland and Wilson, 2005; Yilmaz, 2010). To the authors' knowledge, few studies have so far addressed the consolidation behaviour of field CPB samples (El Aatar, 2009; Fahey et al., 2011; Thompson et al., 2012).

The main objective of the present study is to provide some key knowledge on the effect of consolidation on strength and quality of CPB. Tests are focused on CPB's self-weight consolidation and mechanical behaviour in terms of scale effect and curing conditions. Different CPB mix recipes are prepared with mill tailings sampled from a European and Canadian polymetallic mine. To understand the drainage and settlement phenomena of CPBs, two types of consolidation tests were realized: lab-scale tests via a new tool named the CUAPS (curing under applied pressure system); and in situ-scale tests via columns installed at a paste backfill plant.

2 MATERIAL AND METHODS

2.1 Experimental Setups

To study the CPB's consolidation two types of testing were used: a lab test by applying a pressure on the top of CPB specimen using the improved CUAPS (Fig. 1a); and on-site tests using columns with a 3 m height (Fig. 1b). CUAPS aims to imitate the in situ CPB situation during its placement and curing processes while columns allow simulating the stope backfilling steps and drainage configurations such as undrained columns UD, half-drained HD, and fully-drained FD column. A full description of CUAPS and some preliminary results is entirely provided in Benzaazoua et al. (2006), El Aatar (2009), Yilmaz (2010), and Yilmaz et al. (2010).

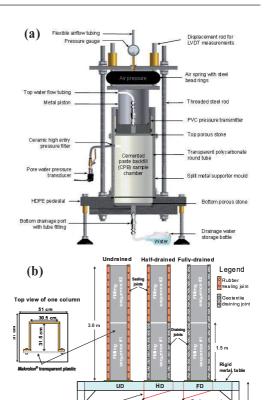


Figure 1. A schematic view of both CUAPS and columns used in the experiments

2.2 Material Characteristics

In the present study, two types of tailings were used from two different mines located in Europe and Canada. For lab testing, CPB mix was prepared by wet tailings filter cake discharged from two vacuum disc filters at a paste backfill plant in Sweden. The tailings' physical properties are listed in Table 1. More details can be found in Benzaazoua et al. (2005). Chemical analyses indicate that tailings sample contains the Si, Mg, Ca, Al, Fe, and S contents of 32.7%, 2.6%, 3.5%, 2.6%, 6.9%, and 4.7% while water contains the sulphate and calcium concentration of 4344 mg/L and 805 mg/L, respectively.

In situ testing was carried out at the paste fill plant of a mine located in Quebec. CPB mixes were generated with slightly deslimed tailings (up to 5% of < 20 μ m particle size), and mix water is the recycled mine process water. Tailings have a sulphur content of 16 to 19 wt%. The specific gravity of tailings was found to be 3.53. Further details can be found in El Aatar (2009).

Table 1. Physical properties of paste tailings

Tailings physical parameters	Value
Specific gravity (SG)	2.96
Specific surface area (m ² /g)	1.90
Initial water content (w%)	15.2
Solid mass concentration (Cm%)	85%
Fines content (minus 20 μm; wt%)	20.6
D ₁₀ (μm), grain size at 10% passing	6.5
D ₅₀ (μm), grain size at 50% passing	68.3
D ₉₀ (μm), grain size at 90% passing	187.4
C_U , coefficient of uniformity	13.4
C_C , coefficient of curvature	2.1
U, coefficient of uniformity	2.6

Portland cement type 10 (PCI) alone and PCI blended with a granulated blast furnace slag (PCI/Slag) were used for lab testing as binding agent. The blended cement PCI/Slag was kept at a 20:80 ratio of PCI and Slag. The binder proportions tested were 3, 5, 7 and 10% by weight of dry cement. Note that 10% of binder is in fact not cost effective but corresponds to the upper limit of binder. For in situ testing, only one-type binding agent which composes of PCI and Slag in a ratio of 20:80 wt% was used. The binder content studied was 4.5 wt%.

2.3 Experimental Procedures

All CPB mixes prepared within the CUAPS setups were cured in a fog room for 28-day curing age. The pressure scenarios practiced during curing were similar to the pressures expected to be developed in an underground stope and listed in Table 2.

Table 2. Pressure applying scenarios

Scenarios	Pressure	Pressure	Equivalent
tested	(psi)	(kPa)	height (m)
#1-1	0	0	0
#1-2	18	125	6.4
#1-3	29	200	10.2
#1-4	36	250	12.7
#2-1	0	0	0
#2-2	27	187.5	9.5
#2-3	43.5	300	15.3
#2-4	54	375	19.1

A strategy for pressure application of labmade CPB samples was followed as follows: the corresponding column heights ($h = p/\gamma$) were calculated from the applied pressures (p) and knowing the CPB wet unit weight γ (19.6 kN/m³). During an initial curing of 24 hrs no pressure was applied, but the pressure was incrementally increased up to 250 kPa (acts as ~13-m stope height) and 375 kPa (acts as 19-m stope height) at preset intervals over 4-day curing.

Table 3 summarizes the in situ-prepared CPB mixture parameter values. The on-site observations showed that the initial slump height of 6.7" could increase by a value of about 1" during its transportation in a pipe line from the backfill plant to underground stopes due to the pipe wall shearing. Three columns are designed in order to reflect the in situ conditions of the CPB materials.

Table 3. Paste backfill mix parameters

CPB mixture parameters	Value
Binder content by mass, $B_{\rm M\%}$	4.5 wt%
Binder content by volume, $B_{v\%}$	5.5% v/v
Sulphur content	16-19 wt%
Specific gravity of tailings (SG)	3.53
Specific surface area of tailings S_v	$1.721 \text{ m}^2/\text{g}$
Solid mass concentration $(C_{\text{M }\%})$	75.8% w/w
Solid volume concentration $(C_{V\%})$	47.3% v/v
Gravimetric water content w%	31.9%
Water-to-cementations ratio (W/C)	7.4

Columns were filled in two sequences of 150 cm over 24 hours. A part of re-mixed CPB was also poured into 6 non-perforated moulds (4" dia. and 8" height) as lab-scale undrained control samples. Columns filled are then maintained under the backfill plant ambient conditions for a total curing time of 45 days. Following the curing ages, columns

were dismantled and each CPB column was cut into 10 blocks which correspond to ten different elevations. From each CPB block, two core samples were taken (total 20 core samples for each column). A total of 60 core samples were then wrapped in paraffin film before being placed in the fog room (at approximately 80% RH and $24^{\circ}\text{C} \pm 2^{\circ}\text{C}$) for final curing ages of 87 days (for FD), 89 days (for HD) and 91 days (for UD).

2.4 Methods

2.4.1 Drainage water collection

Drainage water was collected from the water percolated from lab-made CPB samples at a time interval. 25 hours after the columns are filled, the drainage water was collected from the FD and HD columns and the bleeding water was collected from the UD column. Waters collected were used for geochemical analyses (pH, Eh, sulphates content).

2.4.2 Unconfined compression test

The UCS tests were performed on the entire lab and on-site CPB samples (mould samples in triplicate and core samples in duplicate). Tests were carried out by using a computer-controlled testing machine (MTS Sintech 10/GL) with a load capacity of 50 kN and a deformation rate of 0.0001 mm/min. The length-to-diameter ratio is 2 for all samples.

2.4.3 Geotechnical characterization test

The following physical parameters for each CPB sample were calculated: gravimetric water content $w_g\%$, volumetric water content $w_v\%$,, solid mass concentration $C_{\text{M}\%}$, solids specific gravity G_s , degree of saturation $S_r\%$, void ratio e (porosity n) and specific surface area by mass S_{m} (m²/g).

3 RESULTS AND DISCUSSION

3.1 Effect of Pressure and Settlement on Drainage Properties

Figure 2a shows the percent of water drained from consolidated backfills prepared at 3-10 wt% binder contents (for PCI alone) during curing time. It is evident that, during the first

24 hours, CPB was allowed to settle under no consolidation pressure) and only limited amount of water (3.5-5.5% of total) was recorded to drain off samples. Samples were then cured under the pressure (up to 250 kPa), improving the drainage of water. The drainage of water from CPB was noted to almost level off following a curing age of 26 hours despite the gradual increase in the pressure. The volume of water expelled out of samples appeared to depend on binder with a general trend of a decrease as binder increases. A comparable phenomenon of the CPB's drainage properties is observed for the slag-based binders (Fig. 2b). The degree of water retention would be expected to depend on hydration phases formed in backfill mass regarding the quality of binder used.

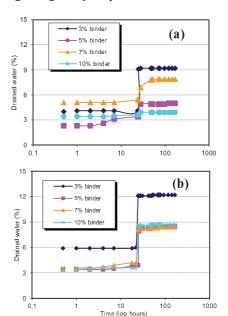


Figure 2. Plot of drainage water vs. time for CPB with PCI alone (a) and CPI/Slag (b)

Figure 3 demonstrates the evolution of cumulative drainage water (Fig. 3a) and the measured consolidation settlement ΔH of the CPB mass (Fig. 3b) since the start of filling the columns. It was observed that, for the total water volume of 160.4 L, only 24 L was collected from the FD column and about 14

L from the HD column reflecting a drainage percentage of 15% and 8.4% respectively. As expected, the drainage capacity of the FD column is twice the one of the HD column. It can be also seen that the observed maximum settlement of CPB (ΔH_{max}) was 16.4 cm for the FD column, 8.5 cm for the HD column and 7.5 cm for the UD column.

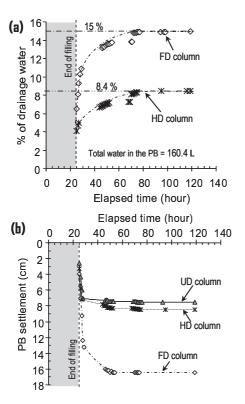


Figure 3. Percentage of drainage water and CPB settlement

The change in initial void ratio (e_0 =1.12) is mainly due to the dissipation of the CPB pore water pressure within the first 50 hours after the end of columns filling. In the case of the UD column the excess pore pressure dissipation is attributed to bleeding at the top of the column. Knowing that each backfill column height was 300 cm, the volumetric strain corresponding to the observed max settlement ΔH_{max} of 16 cm (FD column), 8.5 cm (HD column) and 7.5 cm (UD column) are of 5.5%, 2.8% and 2.5% respectively.

Results show that the behaviour of the UD column is similar to that of the HD column, and the observed strain of the FD backfill is twice the one of the HD and UD columns. This similarity can be explained by a column configuration and their pouring sequencing. The observed in situ CPB stope volumetric strain varies between 3.3% and 5.0%, taking into account a stope height of 30 m. This means that the in situ CPB stopes behave in a similar way than the HD or FD conditions.

3.2 Effect of Binder Type and Content on Physical Properties

Figure 4-5 show the evolution of void ratio and degree of saturation of lab-made CPBs prepared with different binders as a function of CUAPS and mould samples.

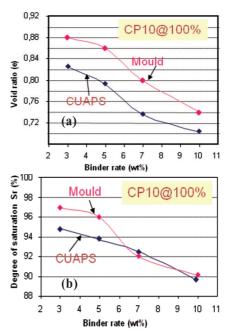


Figure 4. Change in void ratio (a) and degree of saturation (b) of CPB with CPI

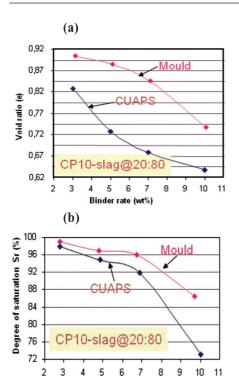


Figure 5. Change in void ratio (a) and degree of saturation (b) of CPB with CPI-Slag

Binder rate (wt%)

From the geotechnical tests undertaken on lab-made CPBs, one can say that void ratio e and the degree of saturation S_r decrease while the specific surface area $S_{\rm m}$ increases with increasing binder content (3- 10 wt% for PCI and PCI/Slag binders). The level of decreasing in S_r was recorded to be in the range of 98-69%. The variation in e and nwas noted to be 0.83-0.57 and 0.45-0.37 respectively at 3-10 wt% binder. In addition, the $S_{\rm m}$ of CPB increased from 3.975 to 14.775 m² g⁻¹, depending on the binder type and amount used. There was no correlation between the CPB performance and water content. Emphasis could be made that values n and $S_{\rm m}$ were strongly affected by the drainage ability of lab-made samples.

Some geotechnical properties of in situ CPB core samples were also evaluated in each elevation for the three columns. Table 4 summarizes the range of variation of the values of geotechnical parameters regarding their initial values. All the columns, CPB exhibit the same shape of G_s profile. It can be observed that specific gravity is almost constant for the first CPB layer of 150 cm thick (mean value of 3.29) and this mean value is lower than one of the second CPB layer (mean value of 3.34). If this reduction in G_s is interpreted as the solid volume change (not its mass) which depends only on the volumetric change of binder, one can say that the CPB lower layer must contain more dissolved binder than its upper layer.

Table 4. Physical parameters of in situ CPB

Physical parameters	First	Final
Water content, w%	31.9	15-25
Solid concentration, $C_{\text{M}\%}$	75.8	80-88
Degree of saturation, Sr(%)	100	70–90
Volumetric water content, θ	0.53	0.30 - 0.41
Void ratio, e	1.12	0.70 - 0.90
Porosity, n	0.53	0.40 - 0.48
Specific gravity SG	3.50	3.25-3.35
Surface area Sv (m ² /g)	1.721	8-13

The variation of the degree of saturation S_r is not easy to interpret. The CPB material in the HD column is less saturated than other columns. It was surprisingly observed that the S_r of CPB in the FD and UD columns exhibits a similar variation. The long-term void ratio e (and porosity n) of CPB in the UD column is approximately constant over the entire CPB column height and is higher than one of CPB in the FD and HD columns. These results corroborate the variation of the UCS value obtained from all the columns paste backfill core samples.

3.3 Effect of Curing Pressure on Strength Acquisition of CPB Samples

Figure 6 shows the difference in the strength development of CPB samples as a function of binder content for two different binder: PCI and PCI/Slag. All the samples' slump was set to 7". The strength of consolidated CPBs containing only Portland cement was lower than those obtained from slag-based binders for binder contents of 3-10 wt% and after a 28-day curing time. The UCS value varies between 237 and 1140 kPa for 100%

Portland cement and between 1104 and 3558 kPa for slag-based binder. One can also say that the strength of unconsolidated CPB was low when compared to consolidated ones.

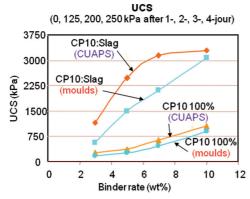


Figure 6. Plot of UCS vs. binder content for CPB cured with and without pressure

For a given binder, the drained backfills produced higher mechanical strengths than un-drained ones after 28 days. This could be attributed to the drainage of excess water in the CPB during consolidation tests, leading to a reduction in porosity and void ratio. It is also expected that the drainage of surplus water affects positively the binder hydration. At 7 wt% binder, the CPB samples prepared with slag-based binder produced 80% and 78% higher strengths respectively than those prepared from Portland cement alone. These results suggest that the CUAPS apparatus may defeat the potential problems associated with in situ CPB performance allowing the determination of optimum conditions such as binder type and quantity for a given CPB application in laboratory tests.

Figure 7 shows the evolution of UCS for consolidated CPB samples containing both PCI alone and PCI-Slag blended binders as a function of incremental pressure during early ages of curing. Two final constant pressures were chosen for two sequential stope paste filling scenarios: $p_v = 250$ kPa for scenario A and $p_v = 375$ kPa for scenario B. Scenario B is actually 50% more of what it is chosen to apply the pressure sequence to the samples in scenario A. It is evident that for 5 wt% binder content, the strength acquisition of

CPB samples containing only the PCI binder in Scenario A is increased from 2.5 MPa to 2.75 MPa when the more pressure is applied to samples, as shown clearly in scenario B. In addition, for CPB samples containing the CPI-Slag binder at a binder content of 7 wt%, the strength gain is increased from 3.1 MPa to 3.25 MPa when the scenario selected is switched from A to B. This indicates the benefits of pressure increment applied to the CPB samples during the early ages of curing.

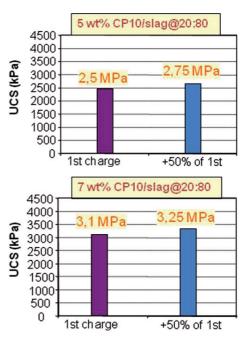


Figure 7. Plot of UCS vs. binder content for CPBs cured under incremental pressures.

The mechanical gain of CPB core samples are also assessed by unconfined compression tests for each elevation in the column (Fig. 8). This figure presents a variation in UCS value of plastic mould CPB samples and the columns CPB core samples as a function of their elevation *z* in each column. One can say that the mechanical gain of CPB samples in the HD and FD column is higher than that of the UD column. The explanation of the UCS variation is directly related to the sequencing of filling and CPB water drainage. Indeed, just after the first filling sequence the CPB

drains a part of its water in the case of the FD and HD columns, but separates from a part of its bleeding water in the case of the UD column. For the second filling sequence, the HD column CPB can drain its water only through the CPB sub-layer of 150 cm thick, while the FD column can drain its water via this layer and the permeable geotextile joint.

Concerning the UD column, the initial bleed water at the top of CPB sub-layer is imprisoned by the new CPB layer and once the column was filled there is again a water separation on the top surface of CPB, a part will evaporate and other will reintegrate the CPB. That means the importance of the sequential filling on the consolidation of the CPB in more of their condition and their configuration of drainage.

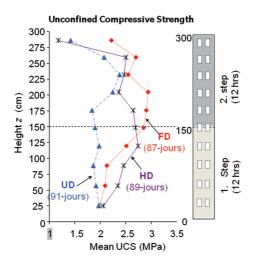


Figure 8. Variation of UCS for CPB core samples as a function of column height

4 CONCLUSIONS

This paper summarizes the final results of an experimental study undertaken to investigate the effect of consolidation on the physical and mechanical performance of laboratory and in situ backfill samples. The laboratory tests were performed by using the improved CUAPS apparatus, while the on-site tests were performed using three settling columns of 3 m high.

The two types of test simulate self-weight consolidation behaviour of CPB material. The CUAPS test simulates the self-weight consolidation of CPB at any elevation of the backfilled stope. However, this kind of test cannot ultimately take into account the effect of the internal pressure or stress transfer and redistribution due to the arching effect and accompanying stress mobilization at the paste backfill-rock interface. The settling column tests will simulate the self-weight consolidation of the entire backfilled stope (prototype) based on small scale model with a scale factor for length (λ =30m / 10m) of 10. These two types of experimentation are therefore complementary.

Based on the results of the present study, the following conclusions can be drawn:

- ➤ Drainage tests revealed that the water separation of CPB samples with slagbased binder is 31% higher than the one made with Portland cement.
- > The geotechnical characterization tests show that, for a given binder type and amount, the void ratio and the degree of saturation of the drained CPBs are lower than those of undrained ones.
- For slag-based binders, the drained CPB samples have produced 51%-7% higher strengths than undrained ones for binder contents of 3-10 wt%. For normal Portland cement, this change remained between 37% and 14% at the same binder ratio.
- ➤ The maximum drainage percentage of 15% and 8% of the total water within CPB was observed for the FD and HD columns. The max measured backfill settlement was 16.4 cm, 8.5 cm and 7.5 cm for the FD, HD and UD column respectively. This corresponds to a volumetric strain of 5.5%, 2.8% and 2.5% respectively.
- ➤ The compression tests results showed that the highest strength was obtained from the FD (2.9 MPa) and HD (2.7 MPa) columns CPB samples. In terms of the physical properties, the specific

gravity and void ratio exhibit a direct dependency of the resulting UCS.

This study has demonstrated that these experimental tests (CUAPS apparatus and settling columns) can be used as valuable tools for the collection of reliable data and the assessment of various conditions on the paste backfill performance in laboratory and on-site tests. These methods may be useful for CPB researchers struggling to understand the physico-mechanical performance of labprepared CPB mixes. Even if CUAPS needs to be improved, depending on applications, so far it has been found to be faster, more practical, and more cost-effective than any other conventional approaches like moulds.

ACKNOWLEDGEMENT

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TKİ - GELİ / YLİ Açık İşletme Göletlerinde Su ve Çevre Rehabilitasyonu

Rehabilitation of Water and Environment of the TKI - GELI / YLI Opencast Mine Lakes

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ÖZET: Maden yataklarının aranması, üretimi ve zenginleştirilmesi süreçlerinde uygulanan işlemler; hava, toprak, su kaynaklarını, dolayısıyla çevreyi ve çevrede yaşayan canlıları etkilemektedir. Kömür açık işletmelerinde üretim çukurlarının dekapaj malzemesiyle doldurulmaması halinde, yüzey suları ve yeraltı su seviyesinin yükselmesiyle büyük veya küçük göletler oluşmaktadır. Düşük pH değeri (asidik karakteristik) ve yüksek metal konsantrasyonu (Fe, Mn, Al, Cu, Pb, Zn vs.) içeren bu göletlerde, baskın halde bulunabilen sülfürlü mineraller (SO₄) ve atık malzemeler, çok önemli çevresel sorunlardan birini oluşturmaktadır. Doğal kaynakların sürdürülebilirliği için, bu tür göletlerin rehabilite edilmesi gerekmektedir.

Bu çalışmada, TKİ - GELİ ve YLİ sahasındaki üç farklı gölette su kirlilik izlemeleri yapılarak, ortalama pH değerleri 6.22-7.79, bulanıklık (NTU) 0.63-6.71, sülfat içeriği 840-1720 mg/L, KOİ 27.2-61.5mg/L ve elektriksel iletkenlik değerleri 1.72-2.71 mS/cm arasında tespit edilmiştir. Belirlenen sonuçlar ilgili yönetmelikler çerçevesinde incelenmiştir. Saha örneklerine ilişkin analizler üç aylık periyotlarla tekrar edilmiştir.

Anahtar kelimeler: Kömür açık işletmeler, asidik maden göletleri, su ve çevre rehabilitasyonu

ABSTRACT: During the search, production and enrichment process of mining operations the air, soil, water resources and living organisms are affected adversely. In coal opencast production, with the rise of surface water and ground water level large or small ponds are composed. The most important environmental problems of these ponds are low pH (acidic characteristic) and high metal concentrations (Fe, Mn, Al, Cu, Pb, Zn etc.) of these ponds, besides the sulfide minerals containing (SO₄) and the waste materials. These ponds needed to be rehabilitated for is one the sustainability of natural resources.

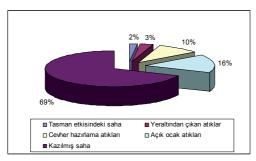
In this study, the average pH values 6.22-7.79, turbidity (NTU) 0.63-6.71, sulphate content 840-1720 mg/L, KOI 2.27-61.5mg/L and electrical conductivity 1.72 -2.71 mS/cm have been measured during the monitoring study of three different lignite opencast mine post-production lakes of the TKI -GELI and YLI. The results were evaluated within the framework of relevant laws and regulations. Analyses were performed in three-month periods.

Keywords: Coal opencast mines, acidic mine lakes, rehabilitation of water and environment

1 GİRİŞ

Madencilik, toplumsal yaşamın en önemli faaliyetlerinden biridir. Madenciliğin amacı, ulusal kalkınma ve ekonomik gelişme için gerekli olan hammaddeleri endüstriye sağlamaktır. Ancak; madencilik faaliyetleri sırasında ve sonrasında kaçınılmaz olarak pek çok arazi bozulmaları, gaz emisyonları, atıklar, toz ve gürültü meydana gelmektedir (Pietsch 1991, Ünver ve Kara 1994). Günümüzde sanayileşme ve hızlı nüfus artışına bağlı olarak hammaddelere olan talep sürekli artmakta, bunun neticesinde söz konusu tahribatlar da yaygınlaşmaktadır.

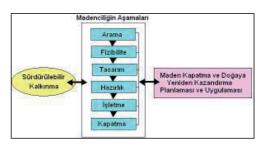
Genel olarak; açık işletme madenciliğinin çevre üzerindeki olumsuz etkileri, yeraltı işletmeleri ve cevher hazırlama çalışmalarına oranla çok daha fazladır. Amerika Birleşik Devletlerinde yapılan araştırmaları yansıtan Şekil 1'e göre, en büyük tahribata açık işletme üretim faaliyetlerinin neden olduğu görülmektedir (Kuzu vd., 1998). Bu durum, madencilik sektöründeki diğer ileri ülkelerde (Kanada, Almanya vb.) olduğu ülkemizde de aynı paraleldedir. Öyle ki; arazi rehabilitasyonu ve çevresel etki değerlendirmesi ile ilgili planlama ve yasal düzenlemelerin büyük bir bölümü, açık işletme madenciliği ile ilgilidir.



Şekil 1. Madencilik faaliyet türlerine göre çevresel etkilerin dağılımı (Delibalta ve Uzal, 2011)

Madencilik faaliyetleri sırasında ve sonrasında çevreye verilen zararları en aza indirgemek için, bütünsel bir maden işletme ve kapatma planlaması uygulamak gerekmektedir (Şek. 2). Söz konusu arazi

rehabilitasyon çalışmaları, mutlaka üretim süreci ile eş zamanlı planlanmalı ve uygulanmalıdır. Ancak bu durumda, madencilik faaliyetleri sürdürülebilir ve doğal çevre ile uyumlu hale getirilebilir.



Şekil 2. Entegre bir maden işletme planlaması ve uygulaması (Düzgün, 2009)

Ayrıca, iyi bir maden kapatma ve doğaya yeniden kazandırma planlaması, ancak ekonomik, sosyal ve çevresel faktörlerin dikkate alındığı sürdürülebilir bir yaklaşımla gerçekleştirilebilir. Bunun için gelişmiş ülkelerde Çevresel Etki Değerlendirmesi (ÇED), Sosyal Etki Değerlendirmesi (SED) ve maddi taahhüt gibi tüm yasal düzenlemeler uygulanırken, gelişmekte olan ülkelerde daha çok ÇED ve doğaya yeniden kazandırma faaliyetleri uygulanmaktadır.

Ülkemizde ilk ÇED yönetmeliği'nin yayınlandığı 1993 yılından itibaren, 2011 yılı sonuna kadar verilen ÇED olumlu kararları sektörel dağılımı Şekil 3'te görülmektedir.

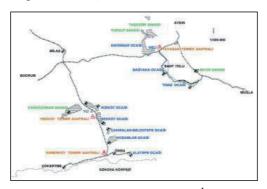


Şekil 3. ÇED olumlu kararları sektörel dağılımı (ÇŞB, 2011)

Bu veriler de bize, ekoloji ve doğal kaynakların korunması için sürdürülebilir bir madencilik-çevre uyumunun gerekliliğini göstermektedir.

2 MATERYAL VE METOT

Yapılan araştırmada deneysel çalışmalar iki kısımda yürütülmüştür. Birinci kısımda, Türkiye Kömür İşletmeleri (TKİ) Kurumuna bağlı Güney Ege Linyit İşletmeleri (GELİ) Müessesesi Yatağan/Muğla ve Yeniköy Linyit İşletmesi (YLİ) Milas/Muğla bölgesinde (Şek. 4) açık işletme sonrası oluşmuş 3 farklı göletten alınan anlık su (Şek. 5) örneklerinde pH, bulanıklık (NTU), sülfat içeriği (mg SO₄/L), kimyasal oksijen ihtiyacı (KOİ, mg/L) ve elektriksel iletkenlik (mS/cm) analizleri yapılarak, belirlenen sonuçlar ilgili yönetmelikler çerçevesinde değerlendirilmiştir.



Şekil 4. Yer bulduru haritası (GELİ, 2012)



Şekil 5. TKİ-YLİ Milas açık işletme göleti su örnekleme çalışması

Söz konusu TKİ-GELİ ve YLİ kömür açık işletme sahalarında bulunan 3 farklı göletten Eylül 2011'de toplam 6 adet temsili numune alınarak, korumalı seyyar soğutucu (termos) içerisinde Niğde Üniversitesi Mühendislik Fakültesi Çevre Mühendisliği Bölümü laboratuvarına getirilmiştir (Şek. 6).



Şekil 6. Laboratuvarda kullanılan cihaz ve yapılan analizlerden bir görünüş

Çalışmalarda analiz edilen parametreler ve ölçüm yöntemleri Çizelge 1'de verilmektedir. Daha sonraki örneklemeler peryodik olarak üç ayda bir, ilk örneklemede belirtilen 3 göletten alınan örnekler üzerinde yukarıda belirtilen analizler yapılarak, su karakterizasyonundaki değişimler izlenmiştir.

Çizelge 1. Çalışmalarda analiz edilen parametreler ve ölçüm yöntemleri

Parametre	Ölçüm Yöntemi	Kullanılan Teçhizat/Cihaz	
pH	SM 4500-H+	pH-metre	
Bulanıklık (NTU)	SM 2130 B	Türbidimetre	
İletkenlik (µmho/cm)	SM 2510 B	İletkenlik-ölçer	
Sülfat (mg/L)	SM 4500 SO ₄ -2 E	Spektrofotometre	

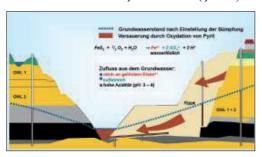
Çalışmanın ikinci kısmında ise; işletme sahasına ait linyit kömürü ve tavan kayaçları (Kireçtaşı, Marn, Kil, Konglomera, Kumtaşı) - taban (Kil, Silt, Mermer) kayaçlarına ait alınan temsili numuneler ile laboratuvarda 1/500 ölçekli kapalı devre yapay gölette simülasyon deneyleri yapılmış, bunun için 80x60x20 cm ebatlarındaki pleksiglas deney havuzu kullanılmıştır (Şek. 7). Alınan temsili su numuneleri ile benzer analizler yapılarak, sonuçlar saha örnekleriyle karşılaştırılmaktadır.



Şekil 7. Kömür açık işletme gölet'i simülasyon deneyinden bir görünüş

3 BULGULAR

Kömür açık işletme sonrası oluşan üretim cukurlarının malzemesiyle dekapaj doldurulmaması halinde, yüzey suları ve yeraltı su seviyesinin yükselmesi ile küçük veya büyük göletler oluşmaktadır. Düşük pH değeri (asidik karakteristik) ve yüksek metal konsantrasyonu (Fe, Mn, Al, Cu, Pb, Zn vs.) göletlerde, baskın halde iceren bu bulunabilen sülfürlü mineraller (SO₄) ve atık malzemeler. doğal kavnakların sürdürülebilirliği için en büyük çevresel sorunlardan birini oluşturmaktadır (Şek. 8).



Şekil 8. Kömür açık işletmelerinde yeraltı suyu etkileşimi (Zschiedrich, 2011)

Asidik maden göletlerinin oluşmasındaki en önemli faktör, kayaç içerisinde bulunan demir sülfürün (pirit, pirotin ve markazit vs.) su ve hava ile teması sonucu okside olmasıdır. Aşağıdaki reaksiyonlara göre oksidasyona uğrayan pirit sonucunda ortaya

çıkan sülfürik asit (hidrojen iyonu) nedeniyle ortamın pH seviyesi düşmektedir.

$$FeS_2(k) + 7/2 O_2(g) + H_2O \rightarrow Fe^{+2}(k) + 2H^+ + 2SO_4^{-2}(s) + _{1S1}$$

$$Fe^{+2}(k) + O_2(g) + 4H^+ \rightarrow Fe^{+3}(k) + 2H_2O + 1S1$$

$$Fe^{+3}(k) + 3H_2O \rightarrow Fe(OH)_3(k)\downarrow + 3H^+$$

$$FeS_{2}(k) + 14Fe^{+3} + 8H_{2}O \rightarrow 15Fe^{+2} + 16H^{+} + 2SO_{4}^{-2}(s) + \iota_{S1}$$

$$FeS_2(k) + 15/4 O_2(g) + 7/2H_2O \rightarrow Fe(OH)_3 + 2H_2SO_4(s) + 1S1$$

Asidik göllerin tipik özelliklerinden olan koyu kahverengi/kırmızı rengi veren ise, reaksiyon sonucu çöken demir hidroksittir. Yukarıdaki reaksiyonların oluşması için oksijen ve suyun varlığı ön şarttır. Fe⁺³'ün kuvvetli bir oksitleyici olması bu reaksiyonlarda büyük bir önem taşımaktadır. Ayrıca, mikroorganizmaların varlığı da reaksiyonları hızlandırmaktadır. Bazı sülfürler asit üretimine yardımcı olurken, kimi karbonat mineralleri (kalsit ve dolomit gibi) nötrleştirici rol oynamakta, bazı silikatlar da tampon etkisi yapmaktadır.

$$CaCO_3(k) + H^+(s) \rightarrow HCO_3^-(s) + Ca^{+2}(s)$$

Asidik ortam oluşumu ve nötrleşmesi burada verilen kimyasal süreçten çok daha karmaşık bir olgudur. Cünkü reaksiyonları bir sekilde hızlandıran, yavaşlatan ve engelleyen çok savıda faktör bulunmaktadır. Maden yatağının jeokimyasal yapısı, işletmeyle teması olan suların asit karakter kazanıp kazanmaması bakımından önemlidir. Dolavisivla, sahanin asit maden drenaii (AMD) üretmeveceğinin üretip saptanabilmesi için, öncelikle yakın sahasının çevresiyle birlikte maden jeolojisine, mineralojisine, üretimzenginleştirme yöntemine, hidrolojisine, topografyasına ve iklimine ait veri tabanının oluşturulması gerekmektedir (Gündüz ve Baba 2009, Karadeniz 2010).

Çalışmanın birinci kısmını oluşturan su karakterizasyon çalışmalarındaki temel amaç, Muğla-Milas ve Yatağan kömür açık işletmelerinde bulunan asit maden göletlerinin mevcut kirlilik durumunun

belirlenmesi ve projenin ilerleyen aşamaları için numune alımında öncelikli göletlerin belirlenmesidir. Bu amaçla bölgede beş farklı göletten örneklemeler yapılmış olup, bu örneklerin analizlerine ait ölçüm değerleri Çizelge 2 ve 3'te verilmektedir.

Çizelge 2. Açık işletme göletleri su analiz sonuçları (1.Ölçüm, Eylül 2011)

Numune Adı	Ölçülen Parametreler							
	рН	İletkenlik (mS/cm)	Bulanıklık (NTU)	Sülfat (mgSO ₄ /L)	KOİ (mgO ₂ /L)			
Milas 1. Gölet	6,46	2,69	1,04	1720	61,5			
Milas 2. Gölet	6,22	1,75	0,63	840	27,2			
Yatağan 1. Gölet	7,59	2,34	1,1	1200	39,2			
Yatağan 2. Gölet	7,16	1,11	79	440	-			
Tınaz Göleti	7,10	2,46	11,7	-	-			

Asit maden göletlerindeki su kirlilik değerlendirme çalışmalarında en önemli parametrelerden olan sülfat değerlerine bakıldığında, en yüksek değerler 1720 mg/L olarak Milas 1.Gölet ve 1200 mg/L olarak Yatağan 1.Göletten alınan örnekler için tespit edilmiştir. Bu değerleri 840 mg/L olarak Milas 2. Göletten alınan örnekler takip etmektedir. Bu nedenle, araştırmanın ilerleyen aşamalarında bu üç göletten örnekler alınarak deneysel çalışmaların sürdürülmesi planlanmıştır (Çiz. 3).

Çizelge 3. Açık işletme göletleri su analiz sonuçları (2.Ölçüm, Aralık 2011)

Numune Adı	Ölçülen Parametreler							
	рН	İletkenlik (mS/cm)	Bulanıklık (NTU)	Sülfat (mgSO ₄ /L)	KOİ (mgO ₂ /L)			
Milas 1. Gölet	7,14	2,71	4,11	1130	58,9			
Milas 2. Gölet	7,41	1,72	6,71	840	29,7			
Yatağan 1.Gölet	7,79	2,29	5,99	1020	41,3			
Yatağan 2.Gölet	7,64	1,97	35,3	900	39,9			
Tınaz Göleti	7,65	1,57	8,78	850	26,7			

Ayrıca; alınan gölet su örneklerinin üç aylık (Eylül, Aralık 2011, Mart 2012) dönemlere göre, metal konsantrasyonlarındaki değişimlerine ait veriler Çizelge 4-6'da özetlenmiştir.

Çizelge 4. Açık işletme gölet suyu metal konsantrasyon analiz sonuçları (1.Ölçüm)

Numune Adı		Ölçülen Parametreler *						
	Al	Ca	Mn	Fe	Cu	Zn	Pb	
Milas 1.Gölet	4,1	497,9	6,1	0,04	8,0	121,9	6,08	
Milas 2.Gölet	0,9	329,8	4,3	0,01	1,3	48,1	1,88	
Yatağan 1.Gölet	35,3	371,6	18,8	0,03	27,2	375,6	2,72	
Yatağan 2.Gölet	32,1	128,7	5,9	0,02	12,3	198,1	1,87	

^{*} Ca (ppm) hariç tüm değerler ppb birimidir.

Çizelge 5. Açık işletme gölet suyu metal konsantrasyon analiz sonuçları (2.Ölçüm)

Numune Adı	Ölçülen Parametreler *						
	Al	Ca	Mn	Fe	Cu	Zn	Pb
Milas	104,	120.6	21.4	728.8	7.2	5.26	104.20
1.Gölet	3	420,6	31,4	/28,8	7,2	5,36	104,30
Milas	6,6	393.6	13.7	646.4	94,2	7.56	6,66
2.Gölet	0,0	393,0	13,7	040,4	74,2	7,30	0,00
Yatağan	0,2	193.5	0.63	579,7	10,1	6.95	0,19
1.Gölet	0,2	193,3	0,03	319,1	10,1	0,93	0,19
Yatağan	0 1	198.4	<dl< td=""><td>584,5</td><td>5,5</td><td>9.06</td><td>9.06</td></dl<>	584,5	5,5	9.06	9.06
2.Gölet	0,1	8,1 198,4	\DL	384,5	3,3	8,06	8,06

Çizelge 6. Açık işletme gölet suyu metal konsantrasyon analiz sonuçları (3.Ölçüm)

Numune Adı	Ölçülen Parametreler *							
	Al	Ca	Mn	Fe	Cu	Zn	Pb	
Milas	62.0	266.6	57.89	1097	20.02	5.60	62.04	
1.Gölet	63,0	200,0	57,89	1097	20,02	5,69	63,04	
Milas	<dl< td=""><td>239.4</td><td>37.11</td><td>608</td><td>85,43</td><td>7.00</td><td><dl< td=""></dl<></td></dl<>	239.4	37.11	608	85,43	7.00	<dl< td=""></dl<>	
2.Gölet	\DL	239,4	3/,11	608	83,43	7,62	\DL	
Yatağan	1.84	267.5	<dl< td=""><td>649</td><td>8.833</td><td>7.39</td><td>1.04</td></dl<>	649	8.833	7.39	1.04	
1.Gölet	1,84	367,5	<dl< td=""><td>649</td><td>8,833</td><td>7,39</td><td>1,84</td></dl<>	649	8,833	7,39	1,84	
Yatağan	0.06	100.4	₹DI	505	5.540	0.06	0.06	
2.Gölet	8,06	198,4	<dl< td=""><td>585</td><td>5,549</td><td>8,06</td><td>8,06</td></dl<>	585	5,549	8,06	8,06	
* C- () h 4" d-¥d hdi								

^{*} Ca (ppm) hariç tüm değerler ppb birimidir.

Çizelge 4-6'da verilen gölet suyu metal analiz sonuçları, Su Kirliliği Kontrolu Yönetmeliği Tablosuna göre yapılan değerlendirmelerde tehlike arz edecek konsanstrasyonlarda olmadığı tespit edilmiş olup, bu suların yine aynı yönetmeliğin Tablo 1: Kıtaiçi Su Kaynaklarının Sınıflarına Göre Kalite Kriterleri parametrelerine göre IV. Sınıf su olarak değerlendirilmiştir (OSİB, 2012).

İşletme koşullarının kontrolü maksadıyla, laboratuarda yapılan simülasyon göleti su analizleri ve metal konsantrasyonlarındaki değişimlerin izlenmesi çalışmalarına ait değerler ise, Çizelge 7 ve 8'de verilmiştir.

Çizelge 7. Açık işletme simülasyon göleti su analiz sonuçları (Eylül, Aralık 2011)

Numune Adı	Ölçülen Parametreler							
	рН	İletkenlik (mS/cm)	Bulanıklık (NTU)	Sülfat (mgSO ₄ /L)	KOİ (mgO ₂ /L)			
Kullanılan Şebeke Suyu	7,50	0,33	0,15	6	0			
Simülasyon 1	7,38	2,70	1,49	1440	33,3			
Simülasyon 2	7,13	3,01	0,48	1700	53,1			

Çizelge 8. Açık işletme simülasyon göleti suyu metal konsantrasyon analiz sonuçları (Eylül, Aralık 2011)

Numune Adı		Ölçülen Parametreler *						
	Al	Ca	Mn	Fe	Cu	Zn	Pb	
Simülasy on 1	<dl< td=""><td>576,5</td><td><dl< td=""><td>639,1</td><td>-</td><td>120,2</td><td>8,63</td></dl<></td></dl<>	576,5	<dl< td=""><td>639,1</td><td>-</td><td>120,2</td><td>8,63</td></dl<>	639,1	-	120,2	8,63	
Simülasy on 2	23,3	635,7	884,3	689,4	-	198,9	7,99	

^{*} Ca (ppm) hariç tüm değerler ppb birimidir.

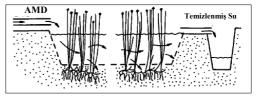
Madencilik faaliyetlerinden etkilenen suların niteliklerinin saptanması hayati önem taşımaktadır. Çünkü çevre mevzuatlarıyla getirilen sınırlamalara uyulmasında, seçilecek arıtma yöntemleri için güvenirlilik ve etkin maliyet, ancak bu şekilde sağlanabilmektedir.

Buna göre; madencilik faaliyetlerinden etkilenen suların genel fiziksel, kimvasal özellikleri acısından isletilen madenin türü başlıca belirleyici olmaktadır. Kömür, baz metal, değerli metal veya bir endüstriyel hammadde olmasına göre suların niteliklerinde büyük farklılıklar görülebilmektedir. Yüksek veva düsük pH, metal ve anyon içeriği yüksek olabilmektedir. Ayrıca, sularda çözünmüş katı, askıda katı konsantrasyonları artabilmekte ve organik kimyasallar bulunabilmektedir.

Sülfürlü cevherler ve değerli metaller AMD ve siyanür sebebiyle farklı değerlendirilse de, madencilik faaliyetlerinden etkilenen suların ortak karakterlerini belirleyen beş ayrı parametreden söz edilmektedir. Bunlar; yüksek veya düşük pH, başta ${\rm SO_4}^{2^-}$ olmak üzere anyonlar, yüksek askıda katı, demir dışı metal, Fe ve Al konsantrasyonları olarak sıralanabilir. Çözünmüş katılar ile toprak alkalileri de bunlara ilave etmek mümkündür.

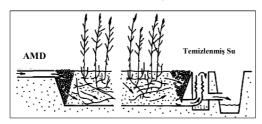
3.1 AMD Arıtma Yöntemleri

Asidik maden drenaji göllerinin yöntem arıtılmasında iki temel kullanılmaktadır. Bunlardan aktif arıtma olarak adlandırılan sistemleri birinci yöntemde, suyun asiditesinin nötralize edilmesi ve çözünmüş metallerin giderimi için suya kimyasal eklenmesi yapılmaktadır. Bu kimyasallar arasında en yaygın olarak kullanılanları, kireç, kostik, dolomit, soda külü ve termik santral külleridir. Pasif arıtma sistemleri olarak adlandırılan yöntemde ise, asidik suyun doğal olarak sulak alanlar vb. sistemler içerisinde iyileştirilmesi hedeflenmektedir (Şek. 9, 10).



Şekil 9. Aerobik (yüzey akışlı) sulak alanın görünümü (Çiftçi ve Akçıl, 2006)

Benzer olarak anoksik kireç drenleri olarak adlandırılan bu kireçtaşının açılan hendeklere doldurulması ve asidik suların da bu hendeklerden geçirilmesi prensibine dayanan teknikler de mevcuttur (Gündüz ve Baba 2009, Karadeniz 2012).



Şekil 10. Anaerobik (yüzeyaltı akışlı) sulak alanın görünümü (Çiftçi ve Akçıl, 2006)

Araştırma sahası TKİ-GELİ ve YLİ açık işletme göletlerinde herhangi bir asidik durumla karşılaşılmadığı için, aktif veya pasif arıtma işlemlerine gerek görülmemiştir. Söz konusu gölet suyu analiz parametreleri IV. sınıf su özellikleri göstermektedir. Dolayısıyla, numunelerin ağır metal konsantrasyonlarına göre, farklı iyileştirme prosesleri planlanabilir.

4 SONUÇ VE ÖNERİLER

İklim ve çevre koruma 21. yüzyılın küresel ölçekte en önemli meselelerinden biri olarak karşımıza çıkmaktadır. Çevre konularının merkezinde ise enerji, su ve iklim politikaları yatmaktadır. Bu durum, tüm sektörlerin enerji temini, su kullanımı ve çevre kirliliği konusunda alması gereken önlemlere büyük bir boyut katmaktadır.

Maden yataklarının aranması, üretimi ve zenginleştirilmesi süreçlerinde uygulanan işlemler; hava, toprak, su kaynaklarını, dolavisiyla cevreyi ve cevrede yasayan canlıları etkilemektedir. Genel olarak, açık işletme madenciliğinin çevre üzerindeki olumsuz etkileri, yeraltı işletmesi ve cevher hazırlama çalışmalarına oranla çok daha fazladır. Madencilik faaliyetleri sonrası yeniden çevrenin bozulan doğaya kazandırılması ve dönüşümü için, çeşitli rehabilitasyon vöntemleri arazi

geliştirilmiştir. Özellikle arazi kullanım planı (ziraat, bayındırlık, rekreasyon, yaban hayatı vs. gibi) yapılacak rehabilitasyonun kapsam ve yoğunluğunu belirlemektedir. Söz konusu çalışmalar, maden üretim süreci ile eş zamanlı planlanmalı ve sürdürülmelidir. Ancak bu durumda, su ve çevre rehabilitasyonu daha ekonomik ve en kısa sürede gerçekleştirilebilir.

Sürdürülen bilimsel araştırma projesi kapsamında, TKİ Kurumuna bağlı GELİ Müessesesi Yatağan/Muğla ve Milas/Muğla sahasındaki 3 farklı göletten alınan örneklerin su kirlilik analizleri yapılarak, belirlenen sonuçlar yönetmelikler çerçevesinde incelenmistir. Yapılan ilk analizlerde üç adet gölet'in ortalama pH değerleri 6.22-7.79, bulanıklık (NTU) 0.63-6.71, sülfat içeriği 840-1720 mg/L, KOİ 27.2-61.5mg/L ve elektriksel iletkenlik değerleri 1.72-2.71 arasında tespit edilmiştir. İncelenen açık işletme göletlerinde herhangi bir asidik durumla karşılaşılmadığı için, aktif veya işlemlerine gerek pasif arıtma görülmemektedir. Ancak, kömür yapısındaki %1.20~2.00 toplam kükürt içeriği, pirit'in oksidasyonu sonucu oluşan kısmen yüksek Fe²⁺ konsantrasyonu ve Su Kirliliği Kontrolu Yönetmeliği Tablosuna göre, söz konusu gölet suyu parametreleri IV. sınıf su özellikleri göstermektedir. Dolayısıyla, gölet örneklerindeki ağır metal konsantrasyonlarına ve kullanım amaçlarına bağlı olarak, farklı iyileştirme prosesleri planlanabilir.

Madencilik faaliyetleri sonrası kısmen bozulan su yapısı ve doğal çevrenin yeniden düzenlenmesi ve iyileştirilmesinde temel amaç, bu arazilerin güzel bir peyzaj görünümü kazanması yanında, eski ekolojik ve ekonomik değerine kavuşturulması veya daha da geliştirilmesi olmalıdır. Çok yönlü disiplinlerarası çalışmayı gerektiren bu faaliyetler, ancak mevcut yasal, ekonomik ve zamansal olanaklar ölçüsünde gerçekleştirilebilir.

TEŞEKKÜR

Bu çalışma; Niğde Üniversitesi Rektörlüğü Bilimsel Araştırma Projeleri Birimince FEB 2011/17 No'lu Proje kapsamında mali yönden desteklenmiştir. Ayrıca, TKİ Kurumu Ar-Ge Daire Başkanlığı tarafından saha çalışmaları izni verilmiştir. Yazarlar, verilen destekten dolayı her iki kuruma da teşekkürlerini sunar.

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A Systematic Approach Applied to Closure and Contingency Plans for Tailings Dams

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ABSTRACT The present work establishes a step-by-step methodology aiming the development of a practical tool in the design of closure and contingency plans of tailings dams. Risk assessment and the foreseeable scenarios in case of a break, based on mathematical models, are mandatory in these plans. Different scenarios of rupture of the dam are established, based on geostatistical methodologies, allowed to build flood maps. These maps allow not only an a priori evaluation of the areas eventually affected and the impact on neighboring populations, but also constitute key elements in the implementation of emergency procedures that must accompany the life of the structure. The developed methodology was applied in Portuguese new project as a case study, revealing a good acceptation by the mine project sponsors as well by the authorities.

1 INTRODUCTION

Tailings dams are critical structures whose project is expected to be buoyed by a compromise between two opposites: low cost versus long life. By one hand tailings dams are intended to store a product without economic value, but on the other they are required for a long duration, since these structures will last long beyond the lifetime of the mine. Nowadays there exist alternatives to tailings disposal, deposition in paste, but as tailings are in the form of pulp with a low percentage of solids, the most economical solution still the tailings dams. Based on the construction method, two types of tailings dams are possible: self-built dams (downstream, centerline, upstream, or a combination of any of the previous); and embankment dams pre-build with inert material. Due to the properties of the built material, self-built tailings dams offer environmental concerns, since its collapse could lead to long term

environmental damage with huge cleanup costs (Chambers, 2011), being the last cited type the best option for new mining projects. Even so, the tailings dams are the central structures in an environmental impact assessment (EIA) study of a mining project. The Portuguese environmental agency (APA), in compliance with the SEVESO (2012/18/EU) requires directives inclusion in the EIA of two separate plans for the tailings dam: the closure plan and the emergency plan. These plans follow the the recommendations of "Best available Commission document techniques for management of tailings and waste-rock in mining activities" as well the United Nations document "Apell for mining - guidance for the mining industry in raising awareness and preparedness for emergencies at local level" which can be seen as a tool for implementing in practice the requirements of the SEVESO directive.

Risk analysis is an integral part of both closure and contingency plans, as these

should be subsequently published and distributed to various entities.

2 METHODOLOGY

2.1 Closure Plan

A closure plan of a tailings dam should be seen as a dynamic object that being developed at the design stage (before the start of mine) can only take a definite character when the ore processing facility stops operating. It starts off as a concept plan to go evolving, following the life cycle of the mine, until it becomes a detailed plan at the closure of the mine. Basically, this is the definition of action plans order to answer the following questions: What should be done? When should it be done? Who are those responsible? What are the resources involved? How much does it cost?, aiming to ensure the physical and chemical stability of the tailings mine facility.

A closure plan should contain a description of the following elements:

- a) Mining enterprise ore deposit, exploitation method, ore processing, rock wastes and tailings;
 - b) Mining closure;
 - c) Tailings dam closure;
 - d) Risk analysis;
 - e) Action plan;
 - f) After-closure monitoring plan;
 - g) Future land use;
 - h) Tailings dam closure cost.

2.1.1 Risk Assessment

Risk management in a structure such as a tailings dam is a process which involves: an assessment of accident hazard - risk analysis, and implementing a program of mitigation and risk control - contingency plan.

Risk analysis includes the identification of sources of danger and the risks they represent in the event of an accident and for the environment (considered in its main compartments: air, water, soil and biota) for both neighboring populations. The risk assessment must be made on a periodic basis, involving processes for the identification of the probability of an

accident. There are several methodologies for risk assessment, namely:

- Process/system checklists;
- System design models;
- Safety reviews;
- Relative ranking;
- Preliminary hazard analysis;
- "What-if" analysis;
- Probabilistic simulation analysis;
- Fault-tree analysis:
- Event-tree analysis;
- Cause-consequence analysis and human error analysis;
- Hazard and operability (HAZOP) studies:
- Failure modes, effects (and critically) analysis (FMEA and FMECA).

For an embankment tailings dam, in the initial project stage, the risk assessment recommended methodology is FMEA/FMECA with inventory of the causes of an possible accident associated to a probability estimated in a qualitative basis versus the severity of the consequences sorted by levels estimated through the environmental assimilative capacity and sensitivity and the local population features (occupation health and safety). occurrence probability of an accident in a qualitative basis is estimated on the history of accidents in similar facilities, on the project of the tailings dam and on the available knowledge of geological, topographical, hydrogeological and weather features of the area.

The potential triggers and failure modes for a tailings dam are:

- Dam overtopping wave action, deregulated water balance;
- Dam instability walls erosion and piping, liquefaction, pore pressure;
- Foundation instability karst beneath dam, subsidence, sliding, seepage, seismic liquefaction of foundations;
- Structural failures piping, pumps fail, pipeline fails, spillways blocked;
 - Power failure.

A FMEA worksheet should be composed by the following columns for each failure mode listed:

1- Failure mode identification code (ID);

Legend

- 2- Failure mode description;
- 3- Possible effects of each failure mode;
- 4- Occurrence probability grade (NL not likely, L low, M moderate, H high, E expected);
 - 5- Mitigation actions;
- 6- Consequences severity grade (N negligible, L-low, M-moderate, H-high, E-extreme). One column for each of the fundamental aspects:
 - a. Direct costs,
 - b. Biological impacts and land use,
 - c. Public concern and image and,
 - d. Human health and safety.

The qualitative grades of probability and consequences severity have correspondence to quantitative ranges as showed in the following tables by Robertson et al. (2003).

Table 1. Likelihood of risk

Likelihood	Safety	Environment
grade	consequences	and public
	(chance of	concern
	occurrence,	consequences
	events/year)	(chance of
		occurrence,
		events/year)
NL-not likely	< 0.01 %	< 0.1 %
L-low	0.01 - 0.1 %	0.1 - 1.0 %
M-moderate	0.1 - 1.0 %	1.0 - 10.0 %
H-high	1.0 - 10.0 %	10.0 - 50.0 %
E-expected	>10 %	> 50 %

Table 2. Severity of effects

Consequences severity	Direct costs
grade	(\$ US)
N – negligible	< \$0.01 M
L-low	\$0.01-\$0.1 M
M – moderate	\$0.1 - \$1.0 M
H – high	\$1.0 – \$10.0 M
E – extreme	> \$10.0 M

The results of this worksheet can be displayed on two dimensional colored risk matrices. The level of risk increases moving from bottom left to the top right, from cold to warm colors, as shown in figure 1.

		Likelihood					
		Not Likely	Low	Moderate	High	Expected	
Consequences severity	Extreme	В				C	
	High						
	Moderate						
nbəsı	Low						
Coi	Negligible	A				D	

:		•				
	A	Trivial ca	ises			
	В	Serious o	lisasters v	with low p	probabilit	у
		(e.g. acc	ident at a	nuclear j	power pla	int)
	С	Serious o	lisasters v	with high	probabili	ty
	D	Frequent	accident	s without	consequ	ences

Figure 1. Risk matrix model.

2.2 Contingency Plan

Contingency and emergency plans are established with the objectives of:

- Containing and controlling incidents so as to minimize their effects, and to limit damage to man, environment and property;
- Implementing the measures necessary to protect man and the environment from the effects of major accidents;
- Communicating the necessary information to the public and to the services or authorities concerned in the area;
- Providing for the restoration and cleanup the environment following a major

Contingency and emergency plans should be reviewed on a periodic basis, tested and widely distributed within the organization and the potentially affected external stakeholders. It should be composed by an action plan, a notification diagram, those responsible for each action, the emergency procedures, a risk analysis, preventing actions and flood maps.

2.2.1 Flood maps - Geostatistical tools

The elaboration of flood maps forced a detailed survey of the topography of the land

surrounding the tailings dam. The basic information in the survey consisted of 27,455.0 geo-referenced records in a regular grid of 50m x 50m. It was identified two small streams.



Figure 2. Topographic survey of the area surrounding the tailings dam.

The more detailed geomorphological modeling of the area was made with the use of geo-statistical methods. Spatial analysis of the continuity was previously performed through the experimental variograms and the respective theoretical model fitting. The interpolation method used for topmorphology modeling was the ordinary kriging without external drift, using a theoretical spherical variogram model without nugget effect (C0 = 0.0), with an inter-level distance of 2,620.0 (C1 = 2,620.0), a range equal to 10,800.0 m (a = 10,800.0 m) a main direction of anisotropy equal to 5 degree (dir = 5°, and W \equiv 0°) and an anisotropy ratio equal to 1.6 (r = 1.6).

$$\gamma(h) = \begin{cases} c_0 + c_1 \left(\frac{3}{2} \frac{h}{a} - \frac{1}{2} \frac{h^3}{a^3} \right) & h < a \\ c_0 + c_1 & h \ge a \end{cases}$$

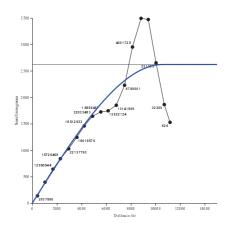


Figure 3. Experimental and theoretical (spherical model) variograms.

2.3 Case Study: A Tailings Dam of a Portuguese Gold Mine Project

The project under study is holding two open pit ore deposits with gold mineralization, located on the vicinities of the Iberian pyritic belt province. The mine has a lifetime of five years and it is expected to extract 1.7 million tons of ore with a grade in gold of 4.5 ppm.

The ore processing plant will produce a gold pre-concentrate through the main unit operations of gravity concentration and froth flotation. To store the tailings from the process plant, tailings dam was designed with a capacity of 2.7 million cubic meters composed by two embankment walls (the main embankment wall of 21 m high by 505 m length and the saddle embankment wall with 15 m high by 430 m length both with slopes of 2.5H:1V in both upstream and downstream sides), taking advantage of the natural topography of the site.

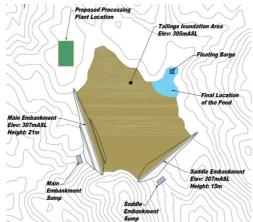


Figure 4. Two embankment tailings dam plant view.

After the mine closure the tailings dam will remain in place, this is justified as the type of construction, foundations and drainage and impervious systems have a definitive character.

Should be highlighted the main elements of the closure and contingency plans of the tailings dam: calculations of the volumes of solids and liquids that come to the dam from ore processing plant over time, the risk analysis and flood maps.

3 RESULTS

3.1 Solid-Liquid Volume Balance

Considering the project data of 39.6 t/h and 75.6 t/h for the mass flow of solids and liquids respectively that feeds the dam, an evaporation of 45%, a precipitation of 750 mm/year and a water reuse of 85% in the first five years, it was possible to estimate the volumes in the tailings dam for a long period after the mine closure. It will raise a steady state after approximately 12 years, as can be seen in Figure 3.

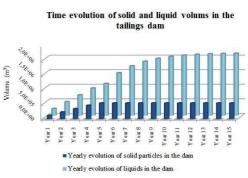


Figure 5. Solid and liquid volumes in the tailings dam from the mine star-up to a 10 years period after the mine closure.

3.2 Risk Assessment Matrices

Risk matrices are based on the failure modes list (FMEA). For the tailings dam in study, that is composed by two embankment walls (the main embankment wall - MEW and the saddle embankment wall - SEW), it was itemized 14 failure modes, as presented in Table 3.

Table 3. Risk worksheet

ID code	Failure mode	Effects
ID01	Collapse of MEW,	Carrying of solid
	affecting foundations	material through
	caused by water	water lines.
	level rise un the	
	stored tailings and/or	
	in foundations.	
ID02	Collapse of SEW,	Carrying of solid
	affecting foundations	material through
	caused by water	water lines.
	level rise un the	
	stored tailings and/or	
	in foundations.	
ID03	Collapse of MEW,	Wall
	affecting foundations	displacements of
	caused by the	large dimension,
	occurrence of an	liquid and solid
	earthquake of degree	material will be
	higher than the	carried by water
	nominal values for	line that may
	the zone or by	reach the nearest

	underestimation of the seismicity.	population.
ID04	Collapse of SEW, affecting foundations caused by the occurrence of an earthquake of degree higher than the nominal values for the zone or by underestimation of the seismicity.	Wall displacements of large dimension, liquid and solid material will be carried by water line that may reach the nearest population.
ID05	Collapse of MEW, without affecting the foundations caused by the occurrence of an earthquake of degree higher than the nominal values for the zone or by underestimation of the seismicity.	Wall displacements of sufficient dimension to carry liquids and solids by water line that may reach the nearest population.
ID06	Collapse of SEW, without affecting the foundations caused by the occurrence of an earthquake of degree higher than the nominal values for the zone or by underestimation of the seismicity.	Wall displacements of sufficient dimension to carry liquids and solids by water line that may reach the nearest population.
ID07	Clogging of drains due to weathering of the embankment, or to the formation of precipitates or to the particle carrying into the drains.	The increase of water flow and pore pressure will collapse (by piping) the inner walls of the dam.
ID08	Clogging of the lower base drainage system due to weathering of the embankment, or to the formation of precipitates or to the particle carrying into the drains.	The increase of water flow and pore pressure will collapse (by depression) the inner walls of the dam.
ID09	Failure of the diversion ditches	The increase of water flow and

	caused by erosion	pore pressure will
	and rupture of water	collapse (by
	management	piping and
	structures in extreme	depression) a
	flood episodes.	located part of
	nood episodes.	dam walls.
ID10	Quality of water	Water discharges
1210	seeping from the	to the two
	waste rock pile	streams located
	located upstream of	downstream of
	the tailings dam	the tailings dam.
	exceeds the limits on	the tainings dam.
	heavy metals as	
	defined by law, due	
	to leaching and/or	
	weaknesses in the	
	impervious layer.	
ID11	Disagreement	Variable.
	between the	
	designed and built,	
	namely: water	
	balance and the grain	
	size properties of the	
	tailings.	
ID12	Failure of	Variable.
	management and/or	
	supervision.	
ID13	Failure of oversight	Variable.
	by regulatory	
	authorities.	
ID14	Intentional damage,	Variable.
	e.g. vandalism,	
	terrorism.	

To each of listed failure modes was attributed a probability level and a grade of consequences severity. For each fundamental aspect: direct costs, biological impacts and land use, public concern and image and, human health and safety a risk matrix was drawn, as showed in the following figures.

	Direct cost	s						
			Likelihood					
		Not Likely	Low	Moderate	High	Expected		
>	Extreme							
Consequences severity	High							
	Moderate		ID01, ID02, ID03, ID04, ID05, ID06					
Consec	Low		ID09, ID10	ID07, ID08				
-	Negligible							

Figure 6. Risk matrix for direct costs.

			Likelihood				
-		Not Likely	Low	Moderate	High	Expected	
	Extreme		ID03, ID04				
Consequences severity	High		ID01, ID02, ID05, ID06, ID09				
	Moderate				ID07, ID08		
Conseq	Low			ID10			
-	Negligible						

Figure 7. Risk matrix for biological impacts end land use.

			Likelihood				
-		Not Likely	Low	Moderate	High	Expected	
x	Extreme						
severity	High		ID03, ID04				
Consequences severity	Moderate		ID01, ID02, ID05, ID06, ID10				
Consec	Low		ID09	ID07, ID08			
_	Negligible						

Figure 8. Risk matrix for Human health and safety.

			Likelihood				
		Not Likely	Low	Moderate	High	Expected	
	Extreme						
seventy	High		ID03, ID04				
nences	Moderate		ID05, ID06				
Consequences severity	Low		ID01, ID02, ID09, ID10	ID07, ID08			
	Negligible						

Figure 9. Risk matrix for public concern and image.

3.3 Different Scenarios

For the tailings dam was considered the possibility of an accident occurring in two distinct periods:

- During the mine lifetime;
- After the closure of mining operations. For any previous circumstances were considered only two possible scenarios:
- First scenario, collapse of the main embankment wall;
- Second Scenario, collapse of the saddle embankment wall.

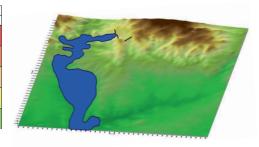


Figure 10. First Scenario, collapse of the main embankment wall.

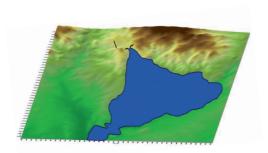


Figure 11. Second Scenario, collapse of the saddle embankment wall.

3.4 Geospatial Representation (3D) of Flood Area

The geostatistical study allowed to the development of flood maps with 108,470.0 data points in a grid of 25m x 25m. Resulting maps with relief modeling, catchment area, intensity and direction of

preferential flow in the event of collapse of the tailings dam.

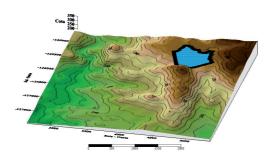


Figure 12. Detailed representation of relief model.

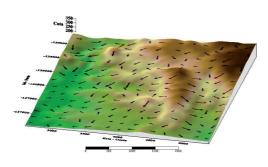


Figure 13. Preferential flow directions and intensity in case of collapse of the tailings dam.

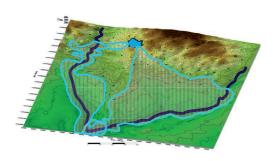


Figure 14. Inundation area in case of collapse of the tailings dam.

4 CONCLUSIONS

The most relevant issues in a tailings dam closure and contingency plans are discussed from the perspective of an integral part of any environmental impact assessment (EIA) and as practical tools to be easily usable by all stakeholders.

Geostatistical tools allowed a more detailed definition of inundation areas, delimiting in space the influence area of the tailings dam.

Given the importance of the risk analysis and flood maps in case of failure, they are here considered key elements in closure and contingency plans.

The risk analysis showed that for the case study biological impacts end land use are the most critical issue to be considered.

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Evaluation of Environmental Performance

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ABSTRACT The assessment of environmental performance has been a concern in business for an extended period of time which increases the frequency of implementation and certification of management systems in this area. A more recent concern has been the inclusion of sustainability issues and the importance of evaluating these within companies as well as their products and processes, taking into account environmental and social effects. This method of assessment generates a solid structure for competitive advantage between various firms in the sector, hence we observe an increase in the study and experimentation of systems for the evaluation of environmental performance in organizations, among them those of the mineral sector. Mining companies can be assessed and classified according to their size, production method and substance exploited. This proposal aims to present and discuss various options for the evaluation of environmental performance indicators, as well as those indicators which are directly associated with the state of Minas Gerais, as it is one of the largest national producers of mineral commodities in Brazil. It will also seek to correlate the evaluation criteria for both open pit mining and underground mining, verifying the advantages and disadvantages of each, domestically and internationally, in strong mining areas. At the end of the study, the aim is to create a cost/benefit comparison analysis for implementing these systems of evaluation, in order to identify the future sustainability in mining. Following on from this, an "ideal" model will be established, which can be applied to ensure optimal performance within businesses with regard to environmental management, taking into account the specific assumptions which may be relevant to the evaluation.

1. ENTERPRISE PERFORMANCE

The performance evaluation within an organization is vital factor for that present high efficiency and effectiveness in its activities. Because of the importance given to this performance the increase is evident in both academic research as well commercially as a way of implementing strategies and goals to be employed to ensure a good performance in the business of the surveyed companies. For those who study these performance measures, it is crucial that they know that management system supports for any decision to be taken. It is also necessary that this management

system take action consistently, after all, a system that acts in a timely manner and / or isolated, tends to get decisions that can lead to confusion, erroneous decision.

Nowadays has been observed a growing concern about the environmental, impacts and consequences that human activity is causing to the environment. The ISO 14000 is a reflection of this concern in the early 90's to ISO saw the need to develop standards of environmental performance to study the standardization of business processes that work with products obtained from nature.

In 1993 the ISO formed a committee with several professionals with the goal of

developing standards involved with the environment, thereby emerged the ISO 14000, which evaluates companies according to compliance with requirements such as:

- Compliance with environmental legislation;
- Personnel trained and qualified;
- Standard procedures and action plans to eliminate or reduce environmental impacts;
- Diagnosis updated environmental aspects of each activity.

To obtain and maintain ISO 14000 certificate, the institution must submit to periodic audits, which are performed by a particular certification company, recognized and accredited by national and international organizations. One of the areas hardest hit with this preoccupation with environment is the mineral sector, sector of ancient origin, and was responsible for the intense social and economic development occurred with the industrial revolution. One aspect that typifies this activity is not being renewable, like most natural resources. The minerals are present mostly in certain locations, according to the characteristics and these geological processes, and tend to exhaust, as they are being withdrawn from nature.

Being an activity where its impacts are easily noticeable visually, mining ends up generating aversion by much of the population, being frowned upon and condemned in most cases. From the 70's the company began to question his way of life, their style polluter and consumer excess. At present mining activity, which was being exercised abusively, without any environmental controls, then began to be monitored and suffer legal restrictions as well as other activities degrading the environment.

2. MINING

2.1 Mining at Brazil

The arrival of the Portuguese in Brazil in the seventeenth century was characterized by the exploitation of Brazil wood, brown sugar,

tobacco, slave labor, which was somewhat retarded the process of finding deposits, as this was not the primary goal of the expeditions. The discovery of gold in the beginning of century XVIII produced the first breakthrough of mining and the emergence of bases that allow the extraction and export of metal. After this period, Brazil experienced a period of decline of this activity, because they believed that deposits are exhausted, come back later to discover new deposits of other minerals too, which would bring back the full force mining activity.

Because of its geological constitution and territorial extent, Brazil is now one of the countries with the highest potential for mineral exploration in the world. Our development has been from the beginning, linked to the exploitation of mineral resources. In 2002, mining activity was responsible for just over 10% of the Gross Domestic Product of the country. Brazil produces almost officially a hundred different minerals present. Nowadays in Brazil there are numerous companies in the mining sector, among these companies, large, medium and small.

Despite being present as self-sufficient in most substances, the country depends on imports as vanadium, potassium, phosphate, sulfur, molybdenum and metallurgical coal

The mineral production has a high multiplier in the economy, leading to a virtuous circle in generating employment and income.

2.2 Mining at Minas Gerais State

The mining activity in the state of Minas Gerais began in the seventeenth century and became known as "Economic Cycle Gold". At the beginning spite of little knowledge in the area of mining, wealth and ease of deposits outweigh its exploitation. The little that is known of mining, was brought slaves from African regions, which had a little knowledge of the area, due to contact with Arab people.

The activity presented predatory actions and violent aggression on the environment and the precarious life of its producers. The authorities at the time did not bother to find solutions to the problems that affected the population, but charges were intense in the and in maintaining privileges. From the nineteenth century we will have the presence of British companies, made some serious investments, which were consolidated as an example of Morro Velho Mining S / A, the only mining still exists. The British firms have introduced new and revolutionary technologies, especially in hydrometallurgical process, which allows the extraction of gold with low degrees of release for the metal. Besides extraction processes by chlorination, for example.

Nowadays, according to data provided by the government of Minas Gerais state is responsible for 44.05% of the Brazilian mineral production, which has increased significantly in the interest of companies to exploit the large reserves of iron ore, diamond, gold, phosphate, zinc, aluminum, limestone and ornamental rocks.

The state is also the largest producer of niobium mineral extensive use in industries due to its superconducting properties. And also in the manufacture of ferro-alloys Nobio, which are employed in the construction of turbines and jet propulsion for aircraft and spacecraft, within other applications.

Mining is considered a strong generator of jobs in the state, and is increasing its importance, because of high investments by businesses, which is increasing more and more in number and areas within the state.

3. ENVIRONMENTAL MANAGEMENT

The Environmental Management System ("EMS") has been increasingly used in companies around the world, environmental protection is not seen more as expense but as an investment in the future. "EMS" models often are at the discretion of each company, which makes an evaluation "good" or "bad", since each firm is restricted to define what

your goals are in order to "collaborate" with the environment.

A factor much discussed in "EMS" is environmental sustainability, which can be related to the concept of eco-efficiency, thus evaluating the ability of a company to reduce its costs and impacts during the many phases of a product until it reaches the consumer.

The mining activity is currently considered a mentor of countless environmental impacts of greater or lesser degree, due to the extraction of minerals, and further processing of these. Mining can cause different impacts according to where it is established.

3.1 Vale's environmental management

Vale S.A is a publicly traded company headquartered in Rio de Janeiro - Brazil and global presence. The company is the largest producer of iron ore and pellets, and second largest producer of nickel, also produce copper, metallurgical coal, manganese, ferroalloys, fertilizers, metals cobalt and platinum group operates in the sectors of logistics, steel and energy.

Vale has an environmental management system with emphasis on mitigation of environmental impacts and prevention of risks associated with its operations. In 2011 spending on environmental protection and control surpassed \$ 1 billion.

Vale recognizes their impacts about climate change, due to the use of coal as an energy source. However, the company has mechanisms that reduce the emission of methane in coal mines as well as commit to invest in research and development for carbon capture and renewable energy investments. The company also promises to reduce emissions by 5% of greenhouse gas emissions, investing in renewable energy sources and achieve the level of 20% biodiesel used in the Brazilian operations.

Vale is one of the first companies to include biodiesel as fuel in its machinery and logistics system as a way to diversify its energy matrix. Assuming the secondary fuel with biodiesel, the company not only

reduces the emission of greenhouse gases, but also recovers impacted areas.

Besides the wide use of renewable energy Vale actively pursues the increase of clean sources of energy, and energy self-sufficiency. One way to achieve these goals is through the construction of dams, which is most of the energy consumed by the company.

Another environmental concern is the company in relation to reuse of water, which was 70% in 2011. In the design of new facilities in Carajás, water is recycled 100% for making concrete and washing of concrete mixer trucks.

In 2011 the size of the area was recovered by Vale of 25.2 km ^ 2 area, equivalent to 2.5 times the Stanly Park in Vancouver, the largest urban park in Canada. One area was in Indonesia, where Vale conducts a recovery work in the region where it is mined zinc. Concerns take into account, how to have the land, prioritizing water drainage, provision of material most fertile areas of rehabilitation and revegetation. The project maintains a source with more than 700,000 trees, which will be used for reforestation of the land.

3.2 Votorantim's Environmental Management

The Votorantim Group was born of a textile factory in 1918. Since then remained in continuous growth and diversification of its activities. In 2001 created the holding company Votorantim holdings, which advanced to the internationalization of its business.

Votorantim Metals focuses on the mining and metallurgy of zinc, nickel and long steel. A solid operating structure ensures the company's performance in the market. Formed by eight industrial plants and mines, located in the states of São Paulo, Rio de Janeiro, Minas Gerais and Goiás, and in Lima, Peru, Votorantim Metals is one of the top five global producers of zinc, the largest manufacturer of nickel electrolyte and Latin American leader in the Brazilian production.

Votorantim has invested in power generation itself since the 1950s, and thus,

the dams as pillars of development. Nowadays the company has about 35 dams that meet 68% of demand for their industries. There is also an investment of different energy sources in order to reduce costs and emissions. In Niquelândia Units (GO) and Tres Marias (MG), replacing fuel oil for electricity production in large scale steam avoided the emission of greenhouse gases.

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In relation the water that circulates through the company's projects, was made viable the construction of a pond, which receives all industrial effluent. After the treatment, this water is used in the production process, reducing the water collection of nearby streams. Besides having also a well of groundwater extraction, which supplies water to areas such as boilers, anodizing and also human consumption.

3.3 Samarco's Environmental Management

Samarco Mining SA is a privately held company whose shareholders in BHP (Billiton Brazil Ltda) and Vale SA, which equally divided control of the company. According to the Ministry of Development, Industry and Foreign Trade, the company won in 2011 the position of fourth largest exporter in Brazil, having plants in the states of Espírito Santo and Minas Gerais.

The company believes that the impact on their areas of influence should be regularly monitored, in order to obtain better results and potentiate economic, environmental and social. These conditions are essential for companies to obtain a license to operate.

Samarco uses in their process of mining thongs which are used to charge 70% of the ore, and ore pipelines for the transportation of the pulp, two systems that reduce fuel consumption, carbon emissions, accident risks, and mitigate impacts such as noise and dust.

The reduction of waste has been a major policy under environmental, for that the company has been working in operations that allow the use of iron ore with increasingly low levels, thus using the ore that was previously considered waste.

With the Master Plan for Water Resources, established in 2011, Samarco plans a seasonal collection of water, which means collecting the water in a given region, according to the natural conditions and availability in the region. Thus, studies are carried out and there is an internal team to define these collections, which are often intensified during the rainy season, when the water volume is higher than normal flow.

In their production process water is used in an integrated manner, the ore pulp ore pipeline after leaving, goes through a process that separates solid from liquid. The solid fraction is then directed to the treatment, while water is led to a treatment system and subsequently a dam, which captures all water generated in operations, thus avoiding water collection of the water bodies near the plant.

As to energy expenditure, Samarco owns the hydroelectric plant Muniz Freire, and has participation in Hydroelectric Plant Guilman-Amorim, which are responsible for about 20% of energy consumption. The rest is acquired by contracts with companies generating energy through hydropower. Therefore, 100% of the energy consumed by the company is from renewable sources. There are also underway, a project to build a thermal power plant in Espirito Santo.

In the Recovery Plan Altered Areas (PRAA), we revegetation in areas of mining and dam. In Minas Gerais, was made the planting of 28 hectares in area Itacolomi State, the city of Ouro Preto and Mariana. This work beyond recovery of vegetation,

also aims at attracting and monitoring of wildlife in rehabilitated areas

3.4 Alcoa's Environmental Management

Alcoa is a privately held company in Brazil, and a world leader in bauxite mining, alumina refining and primary aluminum production and processing. Besides the presence in various states of Brazil, the mining company has operations in 31 countries. In Brazil since 1965, the company operates throughout the aluminum production chain from bauxite mining to production of manufactures.

The main environmental impacts generated in the aluminum industry are related to energy consumption, gases emissions in the atmosphere, including greenhouse gases, the generation of solid waste and excessive water consumption. Accordingly, Alcoa invests in design that tend to minimize these impacts.

Along with bauxite, electricity is one of the main assets for manufacturing aluminum. The company then aims to develop the power generation projects, the construction of dams, and better electrical efficiency in production processes. His goal for the end of 2012 was producing 70% of energy consumed.

In relation to its residues, Alcoa obtained a breakthrough in 2011 when he allowed one of its refinery in the incorporation of fine alumina retained in electrostatic precipitators, the composition of alumina sent to reduce, in order to be transformed into primary aluminum. Thus, about 6mil tonnes of this material are no longer arranged in landfills, significantly reducing the amount of waste.

Were performed in educational campaigns directed to company employees and contractors about saving water, which led to a 12% reduction in consumption in the year 2011. Another initiative to reduce water consumption was the adoption of a closed circuit in the operation of the cooling towers. Accordingly, Alcoa units in Brazil, recycle practically all the water from its production process. In company Pocos de Caldas, Minas

Gerais, there lakes that store rainwater during the rainy season, and this excess is reused in factories.

4 CONCLUSION

The performance evaluation has been a preoccupation in the business for a long time. As it is noted in the environmental management of mining companies listed above, each company works according to their area of expertise, ore mined and tends to look for solutions that mitigate the impacts caused by them.

This assessment system generates a structure of competitive advantage among companies in the same sector, after all it is increasingly necessary to create a model of environmental management within each business so that it can act without harming the environment in which she acts, working toward a world less harmed.

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Annual report Alcoa

Bir Açık İşletmede Doğaya Yeniden Kazandırma Projesi Seçimi Recultivation Project Selection in an Open Pit Mine

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ÖZET Bu çalışmada, Türkiye'de manyezit sektöründe üretim faaliyetleri devam eden bir açık işletme için farklı doğaya yeniden kazandırma proje seçenekleri hazırlanmıştır. Açık işletme madencilik faaliyetleri bittikten sonra, bu açık ocak için üç farklı doğaya yeniden kazandırma seçeneği projelendirilmiştir. İlk doğaya yeniden kazandırma seçeneği açık ocak sahasının kısmen ağaçlandırılıp yapay bir göl olarak kullanılmasıdır. İkinci proje seçeneği, madencilik sonrasında tüm sahanın tamamen ağaçlandırılmasıdır. Sonuncusu ise, madencilik sonrasında alanın çöp ve moloz sahası depolama alanı olarak kullanılmasıdır. Hazırlanan proje alternatifleri yardımıyla en uygun doğaya yeniden kazandırma projesinin seçilebilmesi için bir karar verme süreci oluşturulmuştur. Bu karar verme sürecine etki eden bütün ölçütler belirlenmiş ve hiyerarşik bir yapıya dönüştürülmüştür. Çok Nitelikli Karar Verme yöntemlerinden "Bulanık TOPSIS" yaklaşımı kullanılarak karar verme problemi çözülmüştür. Probleminin çözümünde karar verici olarak madencilik faaliyetlerini yürüten firmada çalışan yöneticiler ve maden mühendislerinden faydalanılmıştır. Bulanık TOPSIS yönteminin madencilikteki farklı karar verme problemlerinin çözümünde karar vericilere yardımcı olabilecek uygun bir yöntem olduğu görülmüştür.

ABSTRACT In this study, different reclamation project alternatives were prepared for an open pit mine that is continuing its production activities in magnesite sector in Turkey. After the end of the open pit mining operations, three reclamation alternatives were projected for this open pit mine. The first reclamation alternative is usage of open-pit mine area as a partly afforested artificial lake. The second one is usage of the post mining area as a completely afforested forest. The last one is usage of the post mining area as a storage space for garbage and debris. A decision-making process was prepared with the help of the project alternatives for selecting the most suitable reclamation project. The entire criteria that affect the decision-making process were identified and transformed into a hierarchical structure. By using Fuzzy TOPSIS which is one of the multi attribute decision making methods, the problem was solved. Managers and mining engineers who are working in the open pit mine and the company's management were evaluated as an expert in the solving process of decision making problem. Fuzzy TOPSIS method was found to be a suitable method that can help decision-makers for solving different decision-making problems in mining.

1 GİRİŞ

Madencilik son dönemde küresel ısınma tehdidi başta olmak üzere birçok olumsuzluk nedeniyle çevreye zarar veren üretim sektörlerinin en başında gelenlerinden birisi olarak değerlendirilmektedir. Açık işletme madenciliği ise, yeraltı maden işletmelerine

nazaran üretim faaliyetlerini daha fazla göz önünde yürüttüğü için çevreye açısından ciddi miktarda tepki çekmektedir. Oysaki madencilik faaliyetleri yapılan alanlarda gerek ekonomik ve gelişmelerin kültürel alanda önemli görüldüğü de bilinmektedir. Elbette ki, bazı alanlarda madencilik faaliyetlerinin çevre için ciddi sorunlar oluşturduğu bilinen bir gerçektir. Ancak, doğaya dost madencilik faaliyetlerini gelişen ve değişen dünya içerisinde birçok farklı alanda görmek de mümkündür. Açık İşletme yöntemi gerekli madencilik yapılan alanlarda önlemler alınmaz ise gerçekten çevreye ciddi verilmektedir. Gerek madencilik faaliyetleri sırasında ve gerekse madencilik faaliyetlerinin bitiminde uygulanacak çeşitli eylem seçenekleri ile çevreye zarar veren uygulamaların en aza indirilmesi sağlanabilmektedir.

Madencilik alanında yapılan çalışmalar incelendiğinde madencilik faaliyetleri sonrasında doğaya yeniden kazandırma başlıklı çeşitli çalışmalar görülmektedir.

Akpınar vd. (1993) açık ocak maden işletmeciliği sırasında bozulan sahaların yeniden düzenlenmesi ve iyileştirilmesi, alan kullanım planlamasının prensipleri, önemi ve aşamalarını inceleyerek kullanım planlama çalışmalarından örnekler vermişlerdir.

Ceylan ve Özkahraman (2000) madencilik faaliyetleri sonucu oluşabilecek çevresel sorunları inceleyerek mevcut sorunların çözümünde uygulanabilecek doğaya yeniden kazandırma seçeneklerini araştırmışlardır.

kazandırma seçeneklerini araştırmışlardır.
Köse ve Pamukçu (2003) ülkemizde faaliyet gösteren mevcut taşocaklarının üretim ve doğaya yeniden kazandırma aşamalarındaki sorunlarına değinerek bunlara teorik çözüm önerileri getirilmesine çalışarak İzmir'de 2 ayrı bölgede bulunan kireçtaşı ocaklarında basamak düzenlemesi ve arazinin restore edilmesi için örnek modeller gelistirmislerdir.

Pamukçu ve Şimşir (2006) İzmir civarında üretim faaliyetleri bitmiş kireçtaşı ocaklarında uygulanabilecek doğaya yeniden kazandırma projesi seçimini bölgesel jeoloji, yeraltı ve yerüstü suyu, flora, iklim ve bölgenin üretim kapasitesi ölçütleri ışığında

değerlendirmişlerdir. Şimşir vd. (2007) dünya literatüründe doğaya yeniden kazandırma süreçlerinde kullanılan terim ve tanımlardan bazılarını açıklayarak, doğaya yeniden kazandırmanın günümüz madenciliğindeki gerekliliği anlatmış ve doğa onarım kavramı ile doğa onarımının aşamalarını detaylı olarak

açıklamışlardır.

Başçetin (2007) Seyitömer Linyitleri İşletmesi açık ocağında kömür üretimi tamamlandıktan sonra uygulanacak en uygun doğaya yeniden kazandırma yöntemi seçiminde Analitik Hiyerarşi Süreci (AHS) yöntemi temelli bir karar modeli kullanmıştır.

Mamurekli ve Tekin (2007) kömür madenciliğinde açık ocak maden işletmeciliğinin çevreye olan etkilerini, arazi düzenleme programının önemini ve aşamalarını ve ülkemizdeki özellikle TKİ'ye bağlı işletmelerde arazi düzenleme çalışmalarını incelemişlerdir.

Düzgün (2009) üretimi bitmiş maden ocaklarının kapatılması ve doğaya yeniden kazandırma uygulamalarını farklı ülkelerdeki uygulamaları ve ülkemizdeki son yasal düzenlemeleri irdeleyerek

değerlendirmiştir.

Pavloudakis vd. (2009) açık ocak maden işletmeciliği yapılan bir linyit ocağında en uygun doğaya yeniden kazandırma projesi seçiminde coğrafi bilgi sistemi ve doğrusal programlama yöntemini kullanarak bölge için en uygun projenin seçilebilmesi için bir karar destek sistemi geliştirmişlerdir.

Cındık ve Acar (2010) faaliyeti bitmiş taş ocaklarının verdiği zararları ve bu alanları doğaya, yöre halkına yeniden kazandırmak için yapılması gerekenleri ve ana hususları

değerlendirmişlerdir.

Bangian vd. (2011) İran'da kömür üretimi yapılan bir açık ocakta doğaya yeniden kazandırma projesi seçiminde Bulanık AHS yöntemini kullanmışlar ve özellikle doğaya yeniden kazandırma maliyetleri üzerine yoğunlaşmışlardır.

Delibalta (2011) farklı ülkelerde yürürlükteki yasal çerçeve kapsamında, madencilik faaliyetleri sonrasında açık işletme yöntemi uygulanan sahaların ekonomik ve ekolojik açıdan yeniden

dönüşümünü incelemiştir.

Kulaksız vd. (2011) ülkemizde beş adet maden sahası için eski maden sahalarının yeniden doğaya kazandırma çalışmalarını örnek sahaları ve bunların uygulamalarını incelemişler ve bu sahalarda ocak içi ve döküm harmanlarının yeniden kazandırma çalışmalarını birlikte değerlendirmişlerdir.

Mallı vd. (2011) açık kömür işletmelerinde dekapaj malzemelerinden oluşan döküm yığınlarının ve üretimini tamamlamış ocak çukurlarının doldurulup doğaya yeniden kazandırılmasını teknik ve ekonomik açıdan incelemişlerdir.

Vujic vd. (2011) Sırbistan'da faaliyet gösteren bir kömür ocağında yapılması planlanan doğaya yeniden kazandırma faaliyetlerini detaylı olarak irdelemişlerdir.

Bu çalışmada, Eskişehir yakınlarında faaliyet gösteren bir Manyezit firmasının üretim faaliyetleri bittikten sonra ruhsat alanında uygulayacağı doğaya kazandırma projesi seçimi Çok yeniden **Nitelikli** Karar Verme yöntemlerinden Bulanı TOPSIS yöntemi kullanılarak incelenmiştir. Bulanık

2 BULANIK TOPSIS YÖNTEMBİLİMİ

Karar verme hem fen bilimleri hem de sosyal bilimler alanında sıklıkla kullanılan bir bilim dalıdır. Hem nitelik hem de nicelik olarak ölçülebilen ölçütlerin değerlendirilmesinde çok farklı karar verme yöntemleri kullanılarak en uygun ve doğru kararların

alınması sağlanabilmektedir.

Literatürde karar verme çok geniş bir uygulama alanı bulmuş bir bilim dalıdır. Karar verme problemlerinin çözümü iki ana grupta incelenmektedir. Bunlar; Çok Amaçlı Karar Verme ve Çok Nitelikli Karar Verme olarak isimlendirilmektedir. Genellikle de bu iki grup birbiri ile karıştırılmaktadır. Eğer bir karar problemi matematiksel olarak ifade edilebiliyorsa Çok Amaçlı Karar Verme, aksi takdirde ise Çok Nitelikli Karar Verme yöntemleri kullanılarak çözülebilmektedir. Karar verme problemlerinin çözümü için geliştirilen birçok Çok Nitelikli Karar Verme yöntemi bulunmaktadır.

Bulanık TOPSIS yöntemi Çok Nitelikli Karar Verme yöntemlerinden bir tanesidir. Bu yöntem kullanılarak alternatif seçeneklerden belirli ölçütler doğrultusunda ve ölçütlerin aldığı bulanık değerler arasında ideal duruma göre karşıla gerçekleştirilmektedir (Chen, 2000). karşılaştırması

Ilk olarak Hwang ve Yoon (1981) tarafından bulunmuş olan bir Çok Nitelikli me yöntemi olan kullanımıyla tercil TOPSIS Verme yönteminin tercih edilen seçeneğin pozitif-ideal çözüme en kısa, negatif-ideal çözüme ise en uzak mesafede bulunması hedeflenmiştir. TOPSIS yönteminde "m" tane seçenek "n" tane ölçüt ile değerlendirilmektedir.

TOPSIS ve Bulanık TOPSIS yöntemindeki temel fark ise dilsel değişkenler ve bulanık üçlü sayıların kullanılmasıdır (Eleren ve

Ersoy, 2007).

2.1 Bulanık Kümeler ve Bulanık Sayılar

Bulanık kümeler kuramı, Zadeh'in klasik matematiksel sistem kuramının yöntemlerinin gerçek dünyadaki pek çok sistemle, özellikle insanları içeren kısmen karmasık sistemlerle uğrasırken vetersiz kalmasından hosnut olmayışından doğmuştur. Bulanık kümeler kuramı, muğlâk ve belirsiz olan problemlerin çözülmesi için geliştirilmiştir. Zadeh'ten bu yana bulanık mantık ve bulanık kümeler kuramı pek çok alanda uygulama bulmuş ve hızla gelişmiştir (Kaptanoğlu ve Özok, 2006).

Bulanık küme, sürekli üyelik derecesine nesneler kümesi küme, Bulanık tanımlanmaktadır. nesneyi 0 ile 1 arasında değişen üyelik derecesine sahip üyelik fonksiyonu ile nitelendirmektedir (Zadeh, 1965). E evrensel kümesinde tanımlanan, bulanık küme A için $\mu_A: E \rightarrow [0,1]$ şeklinde ifade edilir. Bulanık A kümesindeki x elemanı için üyelik

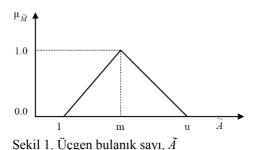
derecesinin gösterimi:

$$A = \{(x, \mu_{A}(x)) | x \in E\}$$
 (1)

şeklindedir (Zimmermann, 1992). μ_A üyelik fonksiyonu [0,1] kapalı aralığında gerçek bir sayıyı göstermektedir (Zadeh, 1975). Bu aralıktaki sayılardan "0" sayısı ilgili aralığında "üyasi olmadığını "1" nesnenin kümenin üyesi olmadığını, sayısı ise ilgili nesnenin kümenin tam üyesi olduğunu belirtmektedir. Bu iki değer arasında bulanan her hangi bir sayı ise ilgini nesnenin kümeye kısmi üyeliğini kümeye üyeliğini göstermektedir.

sayılar Bulanık dışbükey, sınırlı-sürekli normalleştirilmiş, fonksiyonları olan bir bulanık küme olarak ifade edilmektedir. Bulanık sayılar, bulanık kümelerin özel bir alt kümesidir. Yapılan çalışmaya göre farklı bulanık sayıları kullanmak mümkündür. Genelde üçgen ve yamuk olmak üzere iki farklı bulanık sayının uygulamalarda kullanılması söz konusudur. Bu çalışma içerisinde üçgen bulanık sayılar kullanılmıştır.

Üçgen bulanık sayılar, üç tane gerçek sayıyla tanımlanmış bulanık sayıların özel bir çeşidi olup (l, m, u) şeklinde ifade edilmektedir. *l, m* ve *u* parametreleri sırasıyla en küçük olası değeri, en olası değeri ve en büyük olası değeri göstermektedirler. Üçgen bulanık sayı *A*'nın gösterilişi aşağıdakı Şekil 1 ile verilmektedir (Kaptanoğlu ve Özok, 2006).



Üçgen bulanık sayının üyelik fonksiyonu aşağıdaki şekilde tanımlanmaktadır:

$$\mu(w/\tilde{A}) = \begin{cases} 0, & x\langle 1, \\ (x-l)/(m-l), & l \le x \le m, \\ (u-x)/(u-m), & m \le x \le u, \end{cases} (2)$$

$$0, & x\rangle u$$

Üçgen bulanık sayılarda tanımlanmış birçok işlem bulunmakta olup aşağıda bu çalışmada kullanılan işlemler açıklanmıştır. $\tilde{A}_1 = (l_1, m_1, u_1)$ ve $\tilde{A}_2 = (l_2, m_2, u_2)$ iki pozitif bulanık sayı ve k ise pozitif bir gerçek sayı olmak üzere:

$$\tilde{A}_1 \oplus \tilde{A}_2 = (l_1 + l_2, m_1 + m_2, u_1 + u_2)$$
 (3)

$$A_1 \otimes A_2 = (l_1 \cdot l_2, m_1 \cdot m_2, u_1 \cdot u_2)$$
 (4)

$$A \otimes k = (l_1 \cdot k, m_1 \cdot k, u_1 \cdot k) \tag{5}$$

$$\tilde{A}^{-1} = (l_1, m_1, u_1)^{-1} \approx (1/u_1, 1/m_1, 1/l_1)$$
 (6)

Ayrıca iki üçgen bulanık sayı arasındaki uzaklık Vertex yöntemi yardımıyla aşağıdaki gibi hesaplanmaktadır (Öztürk vd., 2008):

$$d_{v}\left(\tilde{m},\tilde{n}\right) = \sqrt{\frac{1}{3}\left[\left(l_{1} - l_{2}\right)^{2} + \left(m_{1} - m_{2}\right)^{2} + \left(u_{1} - u_{2}\right)^{2}\right]}$$
 (7)

2.2 Bulanık TOPSIS Yöntemi

Bulanık TOPSIS yönteminde üçlü bulanık sayılar kullanılmasıyla yapılan çalışmalar ilk kez Negi (1989)'nin doktora teziyle başlamıştır. Ancak, Bulanık TOPSIS algoritmasının eksiklikleri üzerine birçok araştırmacılar çalışmışlardır. Bu araştırmacılardan biri olan Chen (2000) bir çalışmasında bu eksikliği gidermiştir. Bu çalışmada, Chen (2000) tarafından önerilen

yaklaşım kullanılarak dokuz adımda sonuca ulaşılmaktadır.

Yöntemin uygulanmasında 1. Adım Karar verici grubun ve değerlendirme ölçütlerinin belirlenmesidir. Seçim işleminde kullanılacak karar verici grubu seçimin yapılacağı grup olup, bu gruba ait değerlendirme ölçütleri belirlenmektedir. Yöntemin 2. Adımı, her bir ölçütün önem ağırlığı ve önem derecesi için dilsel değirlenler belirlenmesidir. Ifodo yayı dilsel

Yöntemin 2. Adımı, her bir ölçütün önem ağırlığı ve önem derecesi için dilsel değişkenler belirlenmesidir. İfade veya dilsel olarak tanımlanan değerlerden oluşan değişkene "dilsel değişken" denilmektedir. Dilsel değişkenler üçlü bulanık sayılarla ifade edildiği gibi 1, 2, 3, ... şeklinde de ifade edilebilmektedir. Bulanık TOPSIS yöntemi hem nitel hem de nicel ölçütlerin puanlamasıyla uğraşmaktadır. Bundan dolayı çok esnek bir yapıya sahiptir. Yöntemin uygulamasında kullanılacak dilsel değişkenler Çizelge 1 ve Çizelge 2 ile verilmiştir (Chen, 2000).

Çizelge 1. Ölçütlerin önem ağırlığını belirlemede yararlanılan dilsel ifadeler

Simao	Aarldama	Bulanık Sayılar						
Singe	Açıklama	1	m	и				
ED	Çok Düşük	0.0	0.1	0.1				
D	Ďüşük [*]	0.0	0.1	0.2				
OD	Orta Düşük	0.1	0.3	0.5				
O	Orta	0.3	0.5	0.7				
OY	Orta Yüksek	0.5	0.7	0.9				
Y	Yüksek	0.7	0.9	1.0				
EY	En Yüksek	0.9	0.9	1.0				

Çizelge 2. Ölçütlerin değerlerini belirlemede yararlanılan dilsel ifadeler

Cimas	Aarlilama	Bulanık Sayılar						
Sinige	Açıklama	l	m	и				
ÇZ	Çok Zayıf	0	0	1				
ÇZ Ž	Źayıf	0	1	3				
OZ	Orta Zayıf	1	3	5				
O	Orta	3	5	7				
OI	Orta Iyi	5	7	9				
Ĭ	Ivi	7	9	10				
ÇI	Çok İyi	9	9	10				

Karar vericilerin ölçüt ve seçeneklere yönelik yapmış oldukları değerlendirmeler 3. Adımda birleştirilir. Bu işlem için Eşitlik 8 kullanılarak seçenekler için bulanık üçlü sayılar oluşturulur ve Eşitlik 9 kullanılarak ölçütlere ait ağırlık değerleri hesaplanır.

$$x_{ij} = \frac{1}{k} \left(x_{ij}' + x_{ij}^2 + \dots + x_{ij}^k \right) \tag{8}$$

$$W_{ij} = \frac{1}{w} \left(w_{ij}^{l} + w_{ij}^{2} + \dots + w_{ij}^{k} \right)$$
 (9)

burada; k: Karar verici sayısı, w_{ij} : "j" ölçütünün ağırlığı ve x_{ij} : "i" seçeneğinin "j" ölçütünden aldığı değer olarak tanımlanmıştır.

4. Adımda, bulanık karar matrisi ve normalleştirilmiş bulanık karar matrisi oluşturulur. Normalleştirme işlemi yapılırken, Eşitlik 10 kullanılmaktadır.

$$R = \left[r_{ii} \right]_{\text{mon}} \tag{10}$$

burada; i=1, 2,, m ve j=1, 2,, n

$$r_{ij} = \left(\frac{a_{ij}}{c_j}, \frac{b_{ij}}{c_j}, \frac{c_{ij}}{c_j}\right) \text{ ve } c_{ij} = \max c_{ij}$$
 (11)

Ağırlıklı normalleştirilmiş bulanık karar matrisi 5. Adımda oluşturulur. Bu adımda, ağırlıklar ile matrisin elemanlarının çarpımı ile yeni bir matris oluşturulur.

$$V = |v_{ii}|_{x=x} \tag{12}$$

$$v_{ii} = r_{ii} \oplus w_{ii} \tag{13}$$

Bulanık pozitif (A^{+}) ve bulanık negatif (A^{-}) ideal noktalar j=1, 2,, n olmak üzere 6. Adımda tanımlanır.

$$A^{+} = (v_{1}^{+}, v_{2}^{+}, \dots, v_{n}^{+}) \tag{14}$$

$$A^{-} = (v_{1}^{-}, v_{2}^{-}, ..., v_{n}^{-})$$
 (15)

$$v_j^+ = (1, 1, 1)$$
 (16)

$$v_j^- = (0, 0, 0) \tag{17}$$

Seçeneklerin bulanık pozitif ve bulanık negatif ideal çözüme uzaklıkları 7. Adımda hesaplanır.

$$d_{i}^{+} = \sum_{j=1}^{n} d(v_{ij}, v_{j}^{+})$$
 (18)

burada; $i=1,2,3,, m \ ve \ j=1, 2, 3,, n$.

$$d_{i}^{-} = \sum_{j=1}^{n} d(v_{ij}, v_{j}^{-})$$
 (19)

burada; i=1,2,3,...,m ve j=1,2,3,...,n.

Her bir seçeneğin yakınlık katsayısı 8. Adımda aşağıda verilen bağıntı yardımıyla hesaplanır;

$$CC_i = \frac{d_i}{d_i^+ + d_i^-} \tag{20}$$

burada; i=1,2,3,...,m.

Son Adım Yakınlık katsayılarının azalan şekilde sıralanması ile alternatiflerin tercih sırası elde edilmesidir.

$$CC_n > CC_m > CC_k > \dots CC_x$$
 (21)

3 UYGULAMA

Bu çalışmada, Eskişehir ili yakınında faaliyet gösteren Magnesit A.Ş. açık ocağını doğaya yeniden kazandırma için hazırlanan üç farklı proje seçeneği Bulanık TOPSIS yöntemi yardımıyla değerlendirilmiştir.

Magnesit A.Ş. işletmesi; Eskişehir iline 35 km, Bozüyük İlçesine 29 km uzaklıkta olup, Dutluca Köyü' nün yaklaşık 2 km kuzeydoğusunda, maden ruhsatlı sahada bulunmaktadır. Faaliyet yeri, orman mülkiyetindeki arazilerden oluşmaktadır.

Magnesit A.Ş., yabancı sermayeyi teşvik yasası kapmasında 1963 yılında kurulmuştur. Magnesit A.Ş., Türkiye'nin 500 büyük firması içinde yer almaktadır. Magnesit A.Ş., Türk manyezit sektörünün gelişiminde daima bir lokomotif görevi görmüştür. Tesiste gerek ham manyezit ve gerekse sinter manyezit ile harç üretiminde dünyada geçerli en son üretim teknolojisi ve yöntemleri uygulanmaktadır.

Maden üretimi açık ocak işletmeciliği yöntemi ile basamak oluşturularak yapılmaktadır. Maden ocaklarında delme ve patlatma yöntemiyle kazanılan cevherli kütleler son derece modern cevher hazırlama ve zenginleştirme tesislerinde zenginleştirilerek kullanıma hazır hale getirilmektedir.

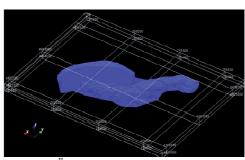
Mevcut tesis alanında, ham manyezit, doğalgaz ve sıvılaştırılmış oksijen kullanılarak düşey fırınlarda (3 adet) ve döner fırında (2 adet) 1750-2000 °C'de pişirilmekte ve sinter manyezit haline getirilmektedir.

3.1 Doğaya Kazandırma **Projesi** Seçenekleri

Magnesit A.Ş.'ye ait ocak ve işletmelerin güncel Google Earth görüntüleri Şekil 2 ile gösterilmiştir. Açık ocaklarda üretim faaliyetleri tamamlandıktan sonra ocak kapatma faaliyetlerine geçileceği zaman olan ocağın planlanan son kalinin NetPno Mine programı ile yapılmış projesi Şekil 3 ile sunulmustur.



Şekil 2. Magnesit A.Ş. açık ocakları güncel görüntüleri



Şekil 3. Üretim faaliyetleri bittikten sonra oluşacak ocağın şekli

Üretim faaliyetleri tamamlandıktan sonra doğaya yeniden kazandırma faaliyetleri ile ilgili farklı proje seçenekleri incelenmiştir. Açık ocak maden işletmesinin yanında, çevher hazırlama ve zenginleştirme tesisleri, fırınlar ve şantiye alanları gibi birçok bileşen çevrenin doğal dengesini bozduğundan fiziksel, kimyasal ve biyolojik etkenler göz önünde bulundurularak; en uygun doğaya yeniden kazandırma projesinin seçim süreci incelenmiştir.

İşletilmesi sona ermiş açık ocakların doğaya yeniden kazandırma amaçlı kullanım olanakları incelendiğinde; tarımsal kullanım, orman amaçlı kullanım, nihai ocak çukurunun göl olarak düzenlenmesi, bina inşa edilmesi, doğal park oluşturulması, çöp veya moloz döküm sahası olarak kullanılması ve hayvancılık yapılması proje yer seçeneklerinin literatürde aldığı görülmüştür (Şimşir vd., 2005).

Mevcut proje seçeneklerinin değerlendirilmesi sonucunda üç proje seçeneklerinin üzerinde çalışmalar seçeneği detaylı

yapılmıştır.

Öncelikle maden sahası ocak çukurunun bir göl şeklinde düzenlenmesi ve çevresinin ağaçlandırılması projelendirilmiştir. Magnesit A.Ş. yetkilileri tarafından da benimsenen proje seçeneğinde işletme içerisinde mevcut binaların korunarak tenis kortları gibi sosyal tesislerin de inşa edilmesi planlanmıştır. Bu amaçla şirket tarafından yaptırılan maketin görüntüsü Şekil 4 ile verilmiştir.

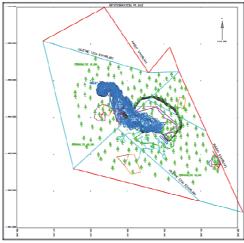


Şekil 4. Magnesit A.Ş. doğaya yeniden kazandırma projesi maketi

Nihai ocak çukurunun bir göl şeklinde düzenlendiği doğaya yeniden kazandırma proje uygulaması için restorasyon planı haritası Şekil 5 ile gösterilmiştir.

İkinci proje seçeneği olarak sahanın orman kullanımı değerlendirilmiştir. amaclı Manyezit A.Ş. halen pasa döküm malzemesini serdiği bazı harmanlara daha önce alınan üst örtü toprağını sererek ağaçlandırma çalışmalarına başlamıştır (Şekil 6). Üretim faaliyetleri tamamlandıktan sonra ocak çukurunun pasa döküm malzemesi ile tesviye edilmesi üzerine lastik tekerlekli yükleyici ile örtü toprağı yayılması planlanmıştır. En üst katına ise stabilizasyonu sağlamak amacı ile üretim faaliyetlerinin başında alınan ve depolanan üst örtü toprağının yine lastik tekerlekli yükleyici ile geri serilmesi sağlanacaktır. Daha sonra ağaçlandırma çalışmaları yapılacak olup tüm bina ve tesisler

kaldırılarak ormanlık alan oluşturulması tasarlanmıştır. Orman amaçlı kullanım için doğaya yeniden kazandırma uygulaması restorasyon planı haritası Şekil 7 ile sunulmuştur.

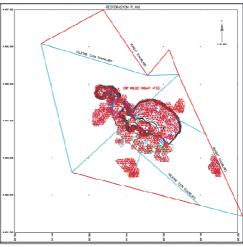


Şekil 5. Göl şeklinde düzenlenen proje seçeneği restorasyon planı haritası



Şekil 6. Manyezit A.Ş.' tarafından yapılan pasa döküm alanın ağaçlandırılma çalışması

Son proje seçeneği olarak ocağın şehir merkezine olan yakınlığından dolayı inşaat merkezine olan yakınlığından dolayı inşaat atığı veya çöp sahası olarak kullanımı şeklinde değerlendirilmesi planlanmıştır. Çöp (moloz) sahası olarak kullanım için doğaya yeniden kazandırma projesinin restorasyon planı haritası Şekil 7 ile gösterilmiştir. Magnesit A.Ş. tarafından cevher üretimi yapılan ocak Eskişehir şehir merkezine yaklaşık olarak 30 km uzaklıkta bulunmaktadır. Bütün şehirlerde istisnaların haricinde görüldüğü gibi Eskişehir'de haricinde görüldüğü gibi Eskişehir'de sürekli olarak batı yönünde büyüme eğilimi göstermektedir. Bu durumda, şirket ocağının konumu çöp veya moloz döküm sahası olarak kullanımı oldukça cazip kılmaktadır.



(moloz) sahası Çöp düzenlenen proje seçeneği restorasyon planı haritası

3.2 Değerlendirme Ölçütleri

Üç farklı proje seçeneğinin Çok Nitelikli Karar Verme yöntemlerinden Bulanık TOPSIS yöntemi ile değerlendirilebilmesi için belirlenen ölçütler aşağıda verilmiştir. Dört ana ölçüt altında 21 ölçüt ile en uygun seçeneğinin belirlenmesine çalışılmıştır. Ölçütler aşağıda verilmiştir;

A- Ekonomik Ölçütler $(\ddot{O}_1 - \ddot{O}_2)$

1. Arazi düzenleme maliyeti (İlk yatırım)

2. İşletme ve bakım maliyeti

B- Bölgesel Ölçütler (Ö₃-Ö₈) 1. Topoğrafya (Yükseklik, eğim, döküm harmanı geometrisi)

2. İklim (Yağış, rüzgâr, nem, ısı, iklim türü, büyüme mevsimi, mikro iklimsel yapı)

3. Hidroloji ve hidrojeoloji (Yüzey ve yeraltı suyu kalitesi değişimi)

Jeoloji (Stratigrafi, yapı, jeomorfoloji, örtü tabakasının kimyasal yapısı)
 Toprak özellikleri (Zirai özellikler-

ekilebilirlik)

6. Ekolojik özellikleri) hayat (Flora-Fauna

C- Doğal Ölçütler (\ddot{O}_9 - \ddot{O}_{16})

Lokasyon (konum) ve ulaşılabilirlik
 Maden ve civarının görselliği

3. Şev durumu (Stabilizasyon ve doğaya özdeş şev oluşturulması)

4. Arazi düzenlenmesi ve toprak serilmesi (Örtü kaplama-arazinin geçirimsiz tabaka ile kaplanması)

5. Vahşi yaşam doğal ortamı oluşturma

- 6. Arazinin erozyondan korunması ve yeniden bitkilendirilmesi
- 7. Arazi mülkiyeti (Orman, zirai ve hazine arazisi)
- 8. Arazi ve çevresinin kullanım şekli D-İdari ve Kültürel Ölçütler $(\ddot{O}_{17}$ - $\ddot{O}_{21})$
 - 1. Yasalar ve yönetmelikler

 - Şirket politikası
 Nüfus kestirimi (Değişimi, dağılımı ve yoğunluğu)
 - 4. Bölge halkı işgücü ve istihdamı
- 5. Bölge halkı eğitim düzeyi ve istekleri. Magnesit A.Ş.'de karar verici olarak bulunan 5 farklı kişiye değerlendirme ölçütleri ve seçenekler ile oluşturulan anket formları verilmiş ve yapılan kısa bir bilgilendirmeden sonra formları doldurmaları istenmiştir. Bulanık TOPSIS uygulanmasında elde edilen anket vönteminin değerler formlarından kullanılmıştır.

3.3 Bulanık TOPSIS Yöntemi ile En Uygun Proje Seçeneğinin Belirlenmesi

Karar verme sürecinin ilk aşamasında, karar vericiler ölçütlerin önemini belirlemek için daha önce Çizelge 1 ile verilen dilsel değişkenlerini kullanmışlar ve bu değerlendirme Çizelge 3 ile sunulmuştur.

Çizelge 3. Ölçütlerin dilsel önem ağırlıkları

Olçüt Ol O2 O3 O4 O5 Ö6 Ö7 Ö8 Ö9 Ö10 O11 O12 O13 O14 Ö15 Ö16 Ö17 Ö18 Ö19 O20 O21	KV1	KV2	KV3	KV4	KV5
O1	ÇY	ÇY	Y	OY	ÇY
O2	ÇD	ÇD	ÇD	OY	Ď
O3	Y	ÇY	ÇY	OD	Y
O4	Y	Y	Y	O	Y
O5	Y	ÇD	Y	O	Y
Ö6	Y	Ď	O	O	Y
Ö7	O	Y	O	O	Y
Ö8	O	Y	Y	O	Y
Ö9	Y	Y	Y	Y	Y
Ö10	OD	Y	ÇY	OY	Y
O11	ÇY	D	ÇΥ	OY	OY
O12	Y	Y	O	OY	OY
O13	ÇD	Y	OY	OY	Y
O14	O	Y	ÇY	Y	ÇY
Ö15	ÇY	D	Ď	O	ÇY
Ö16	O	Y	Y	OD	Y
Ö17	ÇY	ÇY	ÇY	O	ÇY
Ö18	Ó	Y	ĆΥ	Y	ĆΥ
Ö19	ÇY ÇD Y Y Y O O O Y OD ÇY Y CD O CY O CY O CY O CY O CY O CY O C	ÇY ÇD ÇY Y ÇD D Y Y Y Y D Y Y Y Y CY Y Y Y	Y CD CY Y O O O Y CY CY CY CY CY O OY CY O OY CY O OY CY O OY CY O OY CY OY OY OY O	OY OY OD O O O O O O O O O O O O O O O O	CY D Y Y Y Y Y Y Y OY OY CY CY CY CY CY CY CY CY CY CY CY CY CY
O20	ÇD	Y	Y	Y	Y
O21	ÇD	O	O	OY	O

İkinci aşamada, karar vericiler her bir İçüte göre seçeneklerin ağırlığını ölçüte değerlendirmek için daha önce Çizelge 2 ile verilen dilsel değişkenleri kullanmışlar ve yapılan değerlendirme Çizelge 4 ile gösterilmiştir.

Çizelge 4. Ölçütlere göre karar vericiler tarafından verilen üç seçeneğin ağırlıkları

8		*****	*****	*****	*****	*****
Ölçüt	Seç.	KV1	KV2	KV3	KV4	KV5
	A1	Ż	İ	İ	Çİ	ΟZ
Ö1	A2	İ	Z İ	Z İ	ÇZ	Çİ
	A3	ÇZ	I	l	Óİ	ΟZ
	A1	Çİ	Z	ÇZ	Çİ	M
Ö2	A2	İ	İ	Çİ	ÇZ	İ
	A3	ÇZ	Z	ÇΖ	Οİ	M
	A1	Ì	İ	Çİ	Çİ	Çİ
Ö3	A2	ÇZ	Z	Çİ	Çİ	Çİ Oİ
	A3	İ	İ	M	M	OI
	A1	İ	İ	İ	Çİ	Çİ
Ö4	A2	OZ	Z	OZ	M	M
	A3	İ	İ	İ	M	Çİ
	A1	Çİ	Çİ	Çİ	Çİ	Çİ
Ö5	A2	ÇZ	ÇZ	ÇΖ	M	Ż İ
	A3	ÇZ	İ	M	M	İ
	A1	Çİ	Çİ	İ	Çİ	Çİ
Ö6	A2	Ž OZ	ÇΖ	Οİ	M	Ż
	A3	OZ	İ	ÇZ	M	İ
	A1	Z	İ	İ	Çİ	Çİ
Ö7	A2	İ	ÇZ	ÇZ	M	Ž
	A3	Ż	İ	Í	M	Z OZ
	A1	İ	İ	Çİ	Çİ	İ
Ö8	A2	ÇZ	ÇZ	Ź	M	ÇZ
	A3	Z	İ	Ź Çİ	M	Í
	A1	İ	Çİ	İ	Çİ	Çİ
Ö9	A2	M	Ì	İ	M	Çİ
	A3	M	Οİ	Οİ	M	Çİ
	A1	İ	Çİ	İ	Çİ	Çİ
Ö10	A2	ÇZ	CZ	Z İ	M	ÇΖ
	A3	Çİ	Çİ	İ	Οİ	Çİ
	A1	İ	ÇZ	Çİ	Çİ	Çİ
Ö11	A2	ÇZ	ÇΖ	Çİ	M	İ
	A3	İ	İ	Ż	Οİ	İ
	A1	Çİ	Z ÇZ	Ż Çİ	Çİ	Çİ
Ö12	A2	ĊΖ	ÇZ	Ź	M	Ź
	A3	Ž	Çİ	İ	Οİ	Ź Oİ
		CZ	M	Çİ	Çİ	Çİ
Ö13	A1 A2	ÇΖ	Z	ĆZ	M	ÇΖ
	A3	Ž	Z Çİ	Çİ	Οİ	Í
	A1	İ	Ź	İ	İ	İ
Ö14	A2	ÇZ	Z Z Çİ	M	M	Z Çİ
	A3	Ž	Cİ	Çİ	Οİ	Cİ
	A1	ÇZ	Çİ	Ž	İ	Οİ
Ö15	A2	ÇZ	ÇZ	Z Z	M	ÇZ
0.0	A3	ÇZ	Çİ	Z	Οİ	ÇZ
	110	γL	γ.		01	<i>y</i>

Çizelge 4. Ölçütlere göre karar vericiler tarafından verilen üç seçeneğin ağırlıkları (devam)

Ölçüt	Seç.	KV1	KV2	KV3	KV4	KV5
-	A1	Çİ	Çİ	Çİ	İ	Çİ
Ö16	A2	ÇZ	ÇZ	Z	M	ÇZ
	A3	İ	Çİ	Çİ	Οİ	İ
	A1	Çİ	Çİ	Çİ	İ	Çİ
Ö17	A2	ÇΖ	Z	Z	M	M
	A3	Çİ	Çİ	Çİ	M	Çİ
	A1	Çİ	Çİ	Çİ	Çİ Z	Çİ ÇZ
Ö18	A2	ÇΖ	Z	CZ		ÇΖ
	A3	Çİ	İ	ÓΪ	M	Ì
	A1	İ	Çİ	İ	M	İ
Ö19	A2	Ì	M	M	M	ÇΖ
	A3	Z	Çİ	M	M	Ĭ
	A1	Çİ	İ	Çİ	Οİ	Çİ
Ö20	A2	Çİ	M	Οİ	Οİ	ÇZ
	A3	M	Z	İ	Οİ	Ì
	A1	Çİ	M	M	Οİ	Ì
Ö21	A2	ÇZ	M	Z	Οİ	ÇZ
	A3	M	M	M	Οİ	İ

Sonraki aşamada, bulanık karar matrisini oluşturmak için her bir ölçütün bulanık ağırlığını belirlemek için dilsel değerlendirmenin üçgensel bulanık sayılara dönüşümü yapılmıştır. Elde edilen bulanık sayılar yardımıyla her seçenek için bulanık karar matrisleri ve oluşturulmuştur. Oluşturulan bu matrislere öncelikle normalleştirime işlemi uygulandıktan sonra normalleştirilmiş bulanık ağırlıklandırılmış matrisler elde edilmiştir. Her bir seçeneğin sırasıyla bulanık pozitif ideal çözüm ve bulanık negatif ideal çözümden uzaklığının hesaplanması yapılmış ve Çizelge 5 ile verilmiştir.

Çizelge 5. Her bir seçenek için hesaplanan negatif ve pozitif çözümden uzaklıklar

0 1	,	
	Negatif Ideal	Pozitif İdeal
Seçenek	Çözüme	Çözüme
	Uzaklık	Yakınlık
A1	13.434	8.687
A2	6.567	15.330
A3	9.462	10.743

Son aşamada ise hesaplanan negatif ve pozitif çözüme uzaklıklara bağlı olarak hesaplanan yakınlık katsayıları Çizelge 6 ile gösterilmiştir. Yakınlık katsayısına göre, üç seçeneğin sıralama derecesi A1, A2 ve A3 olarak gerçekleşmiştir. Bu durumda, belirlenen ölçütlere ve karar vericiler tarafından yapılan değerlendirmelere göre en uygun seçim A1 kodlu "Maden sahasının gölet olarak kullanımı" seçeneği olmuştur.

Çizelge 6. Hesaplanan yakınlık katsayıları

Seçenek	Yakınlık Katsayısı	Sıralama
A1	0.607	1
A2	0.300	3
A3	0.468	2

4 SONUÇLAR VE ÖNERİLER

çalışmada, Eskişehir ili içerisinde faaliyet gösteren bir Manyezit üreticisinin açık ocağında üretim faaliyetleri tamamlandıktan sonra uygulanabilecek doğaya yeniden kazandırma seçenekleri Bulanık TOPSIS projesi Bulanık TOPSIS değerlendirilmiştir. yöntemi yardımıyla Dilsel ifadelerin kullanılmasıyla gerek ölçütler ve gerekse ölçütler karşısında seçeneklerin aldığı değerler kolayca bulanık sayılara dönüstürülmüş ve son derece gerçekçi bir değerlendirme yapılmıştır. Üç proje seçeneği arasında maden sahasının gölet olarak değerlendirileceği proje seçeneği yapılan degerlendirmeler sonucunda seçenek olarak belirlenmiştir.

Bulanık TOPSIS yönteminin Maden Mühendislerinin karşılaştığı diğer çok nitelikli karar verme problemlerinin çözümünde kullanımının mümkün olduğu görülmüştür. Benzer Çok Nitelikli karar Verme yöntemleri ile karşılaştırıldığında gerek uygulama ve gerekse hesaplama kolaylığı bakımından Bulanık TOPSIS yönteminin son derece avantajlı olduğu görülmektedir.

Bulanık TOPSIS yöntemin veya benzer Çok Nitelikli Karar Verme yöntemlerinin kullanılmasıyla maden mühendislerinin önemli kararları en az hata ile verebilmeleri söz konusu olacaktır.

TESEKKÜR

Bu çalışmaya, bölge madenciliğine ve Maden Mühendisliği eğitimine verdikleri destekten dolayı Magnesit A.Ş. yönetimine bildiri yazarları teşekkür etmektedir.

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Farklı Metalürjik Atıkların Çevresel Açıdan Değerlendirilmesi Assessment of Environmental Impact Potential of Various Metallurgical Wastes

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ÖZET Endüstriyel faaliyetlerin birçoğunda olduğu gibi madencilik, cevher zenginleştirme ve metalurjik işlemlerde de önemli miktarlarda atıklar meydana gelmektedir. Ortaya çıkan bu atıklar genellikle zararlı olup, toprak ve su kirliliği gibi önemli çevresel etkilere neden olabilmektedir. Atıklar depolanırken çevreye potansiyel etkilerini belirlemek için çeşitli fiziksel ve kimyasal testlerden geçirilebilir. Bu çalışmada, pirit külü, bakır curufu, siyanürleme atığı ve borik asit atığı (borjipsi) gibi metalurjik atıklarının çevresel açıdan değerlendirmeleri için TCLP ve SPLP testleri yapılmış ve bu atıkların potansiyel etkileri tartışılmıştır.

ABSTRACT As is in most industrial activities, a considerable amount of waste is generated in mineral processing and metallurgical operations. The waste products in these operations are often hazardous in character and can lead to important environmental problems including soil and water pollution. Various physical and chemical tests are used to determine the potential impact of these wastes on environment when stored in a disposal site. In this study, the leachability tests (TCLP and SPLP) were performed for the environmental characterization of the metallurgical wastes including pyrite ash, copper slag, cyanidation waste and boro-gypsum. Their potential impacts on environment were discussed.

1 GİRİŞ

Diğer birçok endüstriyel faaliyetlerde olduğu gibi madenlerin işletilmesi sonucunda da atıklar meydana gelmektedir (Çetiner v.d., 2006). Madenlerin üretilmesi, cevher zenginleştirme ve metalürjik işlemler sırasında ortaya çıkan atıkların uygun olmayan bir şekilde çevreye bırakılması, hava, toprak ve su kirliği gibi çevre sorunlarına yol açabilmektedir.

Maden, zenginleştirme ve metalürjik proses atıkları atık barajlarında veya sahalarında depolanmaktadır. Bu depolama alanları çok fazla yer kaplamakta ve giderek daralmaktadır. Depolama alanlarına olan gereksinimin ve çevre kirliliğinin azaltılması amacıyla atıkların değerlendirilmesi veya uygun bir biçimde bertaraf edilmesi gerekir. Avrupa'da maden atıklarının depolandığı atık barajlarında meydana gelen kazaların ciddi çevresel sorunlar yaratması, bu konu üzerindeki çalışmaları yoğunlaştırmıştır. Büyük yığınlar halinde veya büyük havuzlarda depolanan zenginleştirme atıkları, bu yığınların kayması, havuzların çökmesi veya barajlarda oluşan çatlamalar sonucu çevre, insan sağlığı ve güvenliği üzerinde ciddi etkilere neden olabilmektedir (Varınca ve Gönüllü, 2006).

Yığınlar halinde veya atık barajlarında depolanan atıkların fiziksel ve kimyasal

duraylılığı oldukça önemlidir. İnce taneli maden atıkları atmosferik koşullardan daha kolay etkilenir; iri boyutlu atıklara nazaran karalılığı daha düşüktür ve alıcı ortamlara daha kolay taşınabilir. Kirlilik, akıntılarla ve nehirler yoluyla taşınabileceği gibi sızma ve süzülme yollarıyla yeraltı sularına karışarak da taşınmaktadır. Orneğin, yağmur suları veya madencilik faaliyetleri sonucu oluşan sular metal salınımına neden olabilir (Güney, 2004). Su kirliliğine sebep olan bazı ağır metaller ve sınır değerleri Çizelge 1'de sunulmuştur. Ağır sıvılar, askıda katı maddeler ve reaktifler de kirletici özelliğe sahip olabilirler.

Atıkların kontrolü konusunda ülkemizde ve dünyada benimsenen atık yönetim stratejisi;

- atıkların kaynağında azaltılması yani az atık üretimi.
- mümkün olduğu durumlarda atıkların tekrar kullanılması,
- atıkların geri kazanımı/dönüşümü şeklindedir (Uzunoğlu, 2007)

Ülkemizde maden atıklarına özgü yönetmelik olmaması nedeniyle bu atıklar özellikle "Tehlikeli Atıkların Kontrolü Yönetmeliği" kapsamında değerlendirilmektedir (Çetiner v.d., 2006). Atıklar, kaynağına, içeriğine, kullanılan üretim ve zenginleştirme teknolojilerine göre değisiklik özelliklere sahiptirler. Bu nedenle Cevre ve Orman Bakanlığı'nda Atık Yönetimi Daire Başkanlığı'na bağlı olarak "Maden Atıkları ve Tehlikesiz Atıkların Yönetimi Şube Müdürlüğü" kurulmustur. Bu Müdürlüğün görevleri maden atıkları ve tehlikesiz atıkların çevre ile uyumlu bir şekilde yönetimini sağlayacak esasları belirlemek ve gerekli düzenlemeleri yapmak olarak belirlenmiştir. Ayrıca Çevre ve Orman Bakanlığı tarafından "Atıkların düzenli depolanmasına ilişkin yönetmelik" taslağı üzerinde çalısmalar devam etmektedir. Bu taslağa göre maden atıkları özelinde ayrı bir yönetmelik yayımlanıp yürürlüğe girene kadar, maden atıkları bu yönetmelik hükmü altına alınmaktadır (RG 2753, 2010).

Maden ve metalürjik atıkların çevresel açıdan karakterizasyonu, bu atıkları potansiyel etlilerinin değerlendirilmesi ve gerekli önlemlerin alınması açısından büyük önem taşımaktadır. Uygulamada kolon testleri, tank testleri ve yerinde testler yapılmakla birlikte genellikle laboratuarda gerçekleştirilen kesikli çalkalama testleri standartlaşmış bulunmaktadır. Atıkların karakterizasyonu için yaygın olarak kullanılan testlerden bazıları şunlardır (Townsend v.d., 2003);

- TCLP-Toxicity Characteristic Leaching Procedure (USEPA Method 1311),
- SPLP-Synthetic Precipitation Leaching Procedure (USEPA Method 1312),
- EP-Tox-Extraction Procedure Toxicity (USEPA Method 1310),
- MEP-Multible Extraction Procedure (USEPA Method 1320),
- WET-Waste Extraction Test (California Code of Regulations),
- ASTM-Extraction Test (ASTM D 3987-85),
- German Batch Leaching Procedure (DIN 38414 S4),
- France Batch Test for Mineral Waste (AFNOR X 31-210),
- Netherlands Standard Leaching Tests (NEN 7341 ve 7349)

Bu testler, depolama alanlarında çevresel faktörlerin etkisivle atıklardan metal salınımının belirlenmesi amacıvla gelistirilmistir. Eğer kontrol edilmesi öngörülen metallerin salınımı belirlenen limit değerlerin üzerinde ise atıklar cevresel acıdan "zararlı" sınıflandırılmaktadır. Bu testlerin sonucuna göre atıklar cevreve uyumlu bir sekilde bertaraf edilmektedirler (Varınca v.d., 2006, Townsend v.d., 2003).

Testler arasındaki temel farklılık; liç çözeltisi, sıvının katı oranı ve ekstraksiyon işleminin süreci ve miktarıdır. TCLP testinde katı atığın açık arazide maruz kalabileceği şartları benzetmek için organik asitle (asetik asit) hazırlanmış çözelti kullanılmaktadır. SPLP testinde ise iki inorganik asitle (nitrik ve sülfürik asit)

hazırlanan çözücü asidik yağmur sularını benzetmek için kullanılmaktadır. TCLP testlerinden elde edilen sonuçlar USEPA tarafından 8 metal için yasal olarak kabul edilen sınırlar için değerlendirilmektedir. SPLP test sonuçları ise genellikle içme suyu standartları ile karşılaştırılmaktadır 2003). (Townsend v.d., Standart yöntemlerde atık malzeme icerisinde bulunmayan veya çok az miktarlarda bulunan tamamının çözünmesi ve durumunda bile limitlere ulasması mümkün olmayan metaller izlenmemektedir.

Katı atıkların uygun yönetim seçeneklerinin belirlenmesi genellikle risk değerlendirmesine bağlıdır. İnsan ve çevre sağlığı temelinde katı atıkların risk yapıldığı değerlendirmesi zaman kirleticilerin yer altı suyuna karışması anahtar haline gelmektedir. Çözünme riskinin değerlendirmek için çok sayıda çözündürme testlerinin geliştirildiğini ve çok farklı atık yönetim senaryosu için yaygın bir şekilde kullanılmaktadır. Cözünme testleri üzerine temellendirilmiş katı atıklar içerisindeki kirleticilerden kaynaklanan risklerin belirlenmesi 4 temel aşamada gerçekleştirilebilir. İlk aşamada TCLP test sonuçları sınır değerleri aşması durumunda tehlikeli atık sınıfına dahil edilerek işlem yapılır. Eğer atık sınır değerlere ulasmayacak sekilde kirlenmeye sebep oluyor ise bu aşamada atık materyal üzerine SPLP testleri uygulanarak elde edilen sonuçlar su kalite standartları ile karşılaştırılarak olası risk değerlendirmeleri yapılmalıdır. Eğer elde edilen değerler standartlarda istenen değerlerden yüksek atıkların sızdırmaz alanlarda depolanmasını gerektirir. Eğer elde edilen çözünme değerleri risk oluşturmuyor ise atığın toplam konsantrasyonu dikkate alınarak tekrar kullanım için değerlendirme vapılabilir. Eğer toplam konsantrasyon doğrudan bosaltım seviyesinden daha az ise bile ilave çözündürme testleri uygulanacak atık yönetimi senaryolarına göre gerekli olabilir. Bu çözündürme testleri pH, sıvı/katı oranı ve zaman gibi özel test koşulları altında gerçekleştirilebilir.

Pirit külü, sülfürik asit üretiminde pirit konsantresinin akışkan yataklı fırınlarda kavrulması sonucu oluşan atıklardır. Sülfürik asit üretiminde, önemli miktarlarda pirit külü (teorik olarak konsantredeki piritin %67'si) çıkmaktadır (Tuğrul v.d., 2005, Tuğrul v.d., 2007, Alp v.d., 2009a). Bakır izabe tesislerinde bakır konsantrelerinin ergitme işlemleri sırasında üretilen yüksek bakır içerikli cüruflar flotasyon işlemi ile temizlenmektedir. Bu tesislerde önemli miktarlarda flotasyon atığı üretilmektedir. Atık depolama alanlarında milyonlarca ton cüruf birikmektedir (Alp v.d., 2008). Borik asit üretim tesislerinde ise kolemanit konsantresi sülfürik asitle işleme sokularak borik asit üretimi yapılmakta ve proses sonucunda oluşan atıklar (borojips) atık barailarına atılmaktadır. cevherlerinin siyanür liçi sonrası yapılan katı-sıvı ayrımı sonucu elde edilen katılar (tesislerin kapasitelerine bağlı olarak yılda yaklaşık 1-2 milyon ton) atık barajlarına atılmaktadır.

Bu çalışmada pirit külü, bakır cürufu, bor jipsi ve siyanürleme atıklarının çevresel açıdan değerlendirmeleri için TCLP ve SPLP testleri yapılmıştır. Elde edilen sonuçlar, bu atıkların olası çevresel etkileri değerlendirilmiştir.

2 MALZEME VE YÖNTEM

2.1 Malzeme

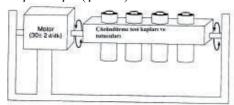
Bu çalışmada; sülfürik asit tesisi atığı pirit külü (PK), bakır izabe tesisi flotasyon atığı olan bakır curufu (BC), borik asit tesisi atığı borojips (BJ) ve siyanürleme tesisi atığı (SA) kullanılmıştır. Söz konusu atıklardan alınan temsili örnekler filtreleme ve kurutma sonrasında örneklenmiştir

2.2 Yöntem

Örneklerin kimyasal bileşimi XRF ve ICP cihazları ile Acme Analiz Laboratuvarında (Kanada), mineralojik bileşimleri Rigaku Geigerflex XRD cihazı ile (20=5-65°) ve

tane boyut dağılımı Malvern Mastersizer (Hydro MU2000) yardımıyla belirlenmiştir.

USEPA TCLP ve SPLP liç testleri, metalüriik atıkların çevresel karakterizasyonu için uvgulanmıstır. TCLP testinde uygun çözücü seçimi pH testlerine göre belirlenmiş ve buna göre, testlerde Çözelti 1 (asetik asit, NaOH ve saf su ile hazırlanan pH değeri 4.93 olan çözelti) kullanılmıştır. SPLP testinde ise 40/60 oranında nitrik/sülfürik asit ve saf su ile hazırlanan ve pH değeri 4,20 olan çözücü kullanılmıştır. Liç testleri plastik kaplarda (200 ml) ve 1/20 katı/sıvı oranında (7,5 g, -1 mm katı ve 150 ml liç çözeltisi) gerçekleştirilmiştir. Örnek kapları hazırlandıktan sonra 30 devir/dk hızla dönen denev düzeneğine yerleştirilmiş ve ters yüz edilecek şekilde 18 saat süreyle karıştırılmıştır (Şekil 1).



Şekil 1. TCLP ve SPLP testlerinin gerçekleştirildiği döndürme/karıştırma cihazı (USEPA, 1997)

Süre sonunda çözelti 0,8 µm filtre kâğıdından süzülerek katısından ayrılmış ve pH'sı ölçülmüştür. Süzüntüden alınan 50 ml örnek içerisine konsantre nitrik asit (3 ml) ilavesi ile çözelti pH'sı ayarlanmış (<pH 2) ve ICP-AES cihazı ile çözünmüş metal içeriği belirlenmiştir. Liç testleri ve analizler paralel olarak yapılmış olup ortalama değerler sunulmuştur. Atıklar içerisinde tamamının çözünmesi durumunda limitlere ulaşmayacağı görülen metaller izlemeye alınmamıştır. Çizelge 1'de verilen elementler için analiz sonucunda elde edilen sonuçlar; TCLP testleri için USEPA limitleri (USEPA, 1997), SPLP testleri için ise içme suyu standart değerleri (TS 266, 1997) ile karşılaştırılmıştır.

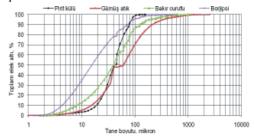
Çizelge 1. TCLP ve SPLP testlerinde kontrol edilmesi öngörülen metaller için limit değerler (TS 266, 1997; Townsend v.d., 2003)

	TCLP	SPLP
Element	US EPA (mg/l)	TS 266 (mg/l)
Ag	5,0	-
Ag Ba	100,0	-
Cr	5,0	0,5
Pb	5,0	0,1
As	5,0	0,1
Mn	´-	0,2
Cu	-	1,0
Ni	-	0,2
Fe	-	0,5

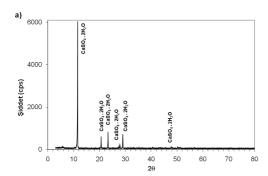
3 BULGULAR VE TARTIŞMA

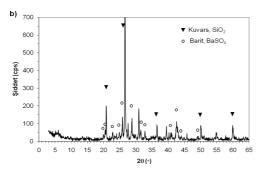
3.1. Atık Malzemelerin Özellikleri

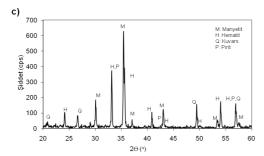
kullanılan calısmada metaluriik atıkların tane boyu dağılımı, mineralojik ve kimyasal bileşimleri karşılaştırmalı olarak sırasıyla Şekil 2, 3 ve Çizelge 2'de sunulmuştur. XRD analizlerinde; BJ'nde CaSO₄.H₂O; SA'nda kuvars ve barit; PK'nde manyetit, hematit, kuvars ve barit, BC'nda fayalit, kuvars ve manyetitin baskın olarak bulunduğu belirlenmiştir. Tane boyut analizlerinde ise %80'inin geçtiği boyut açıklığının BC'nda 80 mikron, PK'nde 60 mikron, SA'nda 140 mikron ve BJ'de 45 mikron olduğu görülmektedir. BJ atıkları oldukça ince taneli, potansiyel kirletici olarak nispeten yüksek oranda As ve B₂O₃ içermektedir. PK, SA ve BC başta As olmak üzere ve değişen oranlarda Pb, Cr, Zn ve Cu içermektedir.

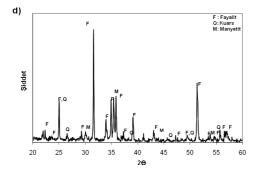


Şekil 2. BJ, SA, PK ve BC'nun tane boyut dağılımları









Şekil 3. BJ (a), SA (b), PK (c) ve BC (d)'na ait XRD grafîkleri

Çizelge 2. Deneylerde kullanılan metalürjik atıkların kimyasal bileşimi

ikianın kimyasan öneşimi											
%	BJ	SA	PK	BC							
SiO_2	9,89	50,69	6.71	30,60							
Al_2O_3	1,92	7,30	1.91	2,96							
Fe_2O_3	0,79	5,72	86.50	59,08							
CaO	33,30	6,77	0.59	0,66							
MgO	2,26	2,94	0.48	0,92							
SO_3	47,60	5,17	1.38	1,01							
Na_2O	0,06	0,00	0.11	0,01							
K_2O	1,15	2,13	0.13	0,48							
P_2O_5	0,03	0,24	0.02	0,03							
TiO_2	0,11	0,20	0.12	0,13							
SrO	1,82	0,15	-	0,01							
Cr_2O_3	-	0,03	0.01	0,06							
MnO	0,02	1,43	0.01	0,03							
PbO	-	1,40	0.02	0,29							
NiO	-	0,01	0,01	-							
CuO	-	0,03	1.34	0,63							
ZnO	0,01	2,89	0.16	2,52							
BaO	-	9,86	0.03	0,10							
Co_2O_3	-	-	0.33	0,06							
As_2O_3	0,60	1,54	0,13	0,02							
ZrO_2	-	0,011	0,01	0,01							
$\mathrm{Sb}_2\mathrm{O}_3$	-	0,84	-	-							
MoO_3	-	-	-	0,08							
B_2O_3	2,80	-	-	-							
Ag_2O	-	0,05	-	-							
Cl	0,01	0,03	0.01	0,03							
F	0,47	0,57	-	0,30							
S	-	0,11	0,41	0,40							
H_2O	17,83	-	-	-							

3.2. TCLP ve SPLP Test Sonuçları

TCLP testinde özellikle Cr, Ba, Ag, Pb ve As elementlerinin konsantrasyonuna bağlı olarak atıklar değerlendirilmektedir. TCLP test sonuçlarına bakıldığında (Çizelge3), bu elementlerin salınımının US EPA sınır değerlerinin altında gerçekleştiği bulunmuştur (Şekil 3). Sonuç olarak bu atıklar çevresel açıdan "zararsız" olarak sınıflandırılabilir. Ancak, özellikle BJ ve

SA'ndan As salınımının yüksek olduğu ve kontrol edilmesi gerektiği görülmektedir. Benzer olarak, PK ve BC'nun Co, Cu ve Zn gibi ağır metaller bakımından kirlilik kaynağı olabileceği görülmektedir. Testler sonucunda pH değişimine bakıldığında ise PK ve BJ' nin ekstraksiyon sıvısı ile muamelesi sırasında başlangıçtaki pH'ın düştüğü, BC ve SA'nın pH'ının ise yükseldiği gözlenmiştir.

Çizelge 3. TCLP test sonuçları

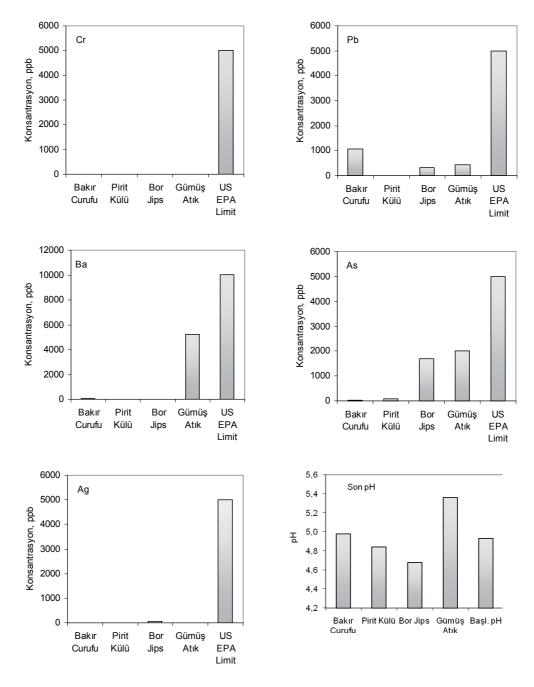
TCLP													pН	pН
(ppb)	Co	Ni	Cu	Ag	Fe	Ti	Cr	Zn	Ba	Mn	Pb	As	ilk	son
BC	439,2	51,3	79749,2	0,8	535,4	4,5	2,0	32769,1	65,6	285,7	1075,2	19,3	4,93	4,98
PK	2365,9	39,5	90091,8	1,2	394,4	10,1	3,2	6634,4	19,1	291,4	3,2	95,2	4,93	4,84
BJ	27,3	76,3	23,8	66,6	409,3	22,6	14,1	284,0	8,9	1073,1	309,3	1695,3	4,93	4,68
GA	14,6	48,7	284,0	4,6	34,6	9,3	11,9	136043,6	5224,3	6081,0	425,4	2006,9	4,93	5,36

SPLP testlerinde kullanılan liç ortamı, karakteristik olarak asidik yağmur sularına benzer ve bu nedenle atmosferik koşullarda depolanan atıkların yağmur sularının etkisi altındaki davranışının kestirilmesine olanak sağlar. Çizelge 4'te özetlenen SPLP test sonuçları Şekil 4'te TS 266 sınır konsantrasyonları ile karşılaştırmalı olarak sunulmuştur. Buna göre atıkların yüzey ve yeraltı sularını kirletebileceği dolayısıyla kontrollü bir bicimde depolanmaları gerektiği görülmektedir.

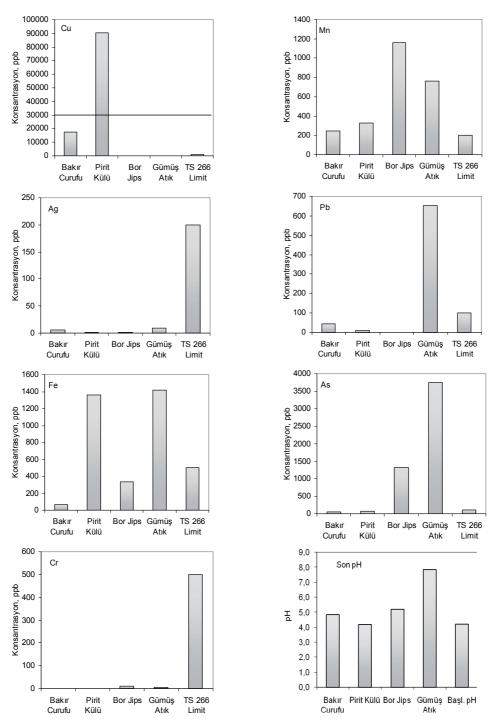
Metalürjik atıkların tekrar kullanılması ve geri kazanımı/dönüşümü, bu atıkların çevresel etkilerinin ve atık yönetimi maliyetlerinin azaltılması bakımından büyük öneme sahiptir. Bununla ilgili olarak özellikle son yıllarda araştırmalar hızla artmıştır. Alp vd (2008, 2009a) tarafından yapılan çalışmalarda, pirit küllerinin ve bakır cüruflarının çimento üretiminde demir kaynağı olarak kullanılabileceği endüstriyel ölçekli testlerde ortava Benzer borojips konmustur. sekilde, atıklarının çimento sanayinde kullanımına yönelik yürütülen araştırmalarda, bunların alçı taşı yerine priz ayarlayıcı olarak kullanılabileceği bulunmuştur (Alp v.d., 2009b)

Çizelge 4. SPLP test sonuçları

SPLP													pН	pН
(ppb)	Co	Ni	Cu	Ag	Fe	Ti	Cr	Zn	Ba	Mn	Pb	As	ilk	son
BC	456,7	46,3	17212,8	6,1	65,1	0,9	-	29492,4	44,8	244,0	45,1	61,8	4,20	4,85
PK	2700,4	37,3	90497,6	1,3	1361,7	3,8	-	7086,4	13,7	328,3	9,0	64,2	4,20	4,18
BJ	23,4	72,0	9,6	0,7	336,4	19,3	9,9	148,5	15,1	1160,4	0,0	1313,4	4,20	5,20
GA	1,8	5,7	32,4	9,6	1418,3	4,0	5,8	3628,6	1693,2	760,7	653,2	3751,8	4,20	7,85



Şekil 4. TCLP testlerinde kontrol edilmesi öngörülen metallerin metalürjik atıklardan salınımı ve USEPA limit değerleri ile karşılaştırılması



Şekil 5. SPLP testlerinde çeşitli metallerin salınımı ve TS 266 değerleri ile karşılaştırılması

4 SONUÇLAR

Metalürjik atıklar, cevher özelliklerine ve metalürjik işlemlere bağlı olarak değişen oranlarda metaller içerir ve bu nedenle genellikle potansiyel kirlilik kaynağı durumundadırlar. Bu çalışmada, pirit külü (PK), siyanür liçi atıkları (SA), borojips (BJ) ve bakır cürufu (BC) atıkları üzerine TCLP ve SPLP testleri uygulanarak, çevresel açıdan değerlendirilmiştir. TCLP sonuçları, kontrol edilmesi öngörülen metaller bakımında bu atıkların "zararsız" olarak sınıflandırılabileceğini göstermiştir. Ancak, SPLP test sonuçları da dikkate alındığında, atıklardan As başta olmak üzere Cu, Zn, Pb gibi ağır metallerin salınımının nispeten yüksek olduğu ve bu ağır metaller bakımından atıkların potansiyel kirlilik kaynağı olabileceği görülmüştür.

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