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# Investigation the applicability of eggshell for the treatment of a contaminated mining site

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ABSTRACT

Acid mine drainage (AMD) is a major environmental problem particularly for abandoned mining site, and many approaches and techniques have been developed for its management and rehabilitation. The abandoned Çan lignite basin enriched with sulfur minerals bearing rocks located in the NW Turkey, and its vicinity has been known as an AMD contaminated mining site for fifty years. Therefore, in order to investigate the applicability of eggshells for rehabilitation of this region, acidic water and solid samples were collected from acidic ponds and waste deposits for performing laboratory experiments. Besides sampling, pH and conductivity were also measured from different acidic ponds, and they are generally around 3 and 5717 μS/cm, respectively. In addition, the dissolved heavy metals as contaminants have been identified. In order to remove heavy metals and other pollutants from these contaminated ponds and stop further AMD generation, the grinded eggshell (−0.125 mm) was used as a low-cost material in batch experiments and column tests. During batch tests, the effects of the amount of the eggshell, the amount of contaminated water and contact time on adsorption were investigated by monitoring rising in pH value until 6.5, as well as by comparing initial and final concentrations of dissolved contaminants. Consequently, after all of testing and related analyses, the required amount of eggshells was determined for acidic ponds found at abandoned Çan mining site. The outcomes of the present study reveal the applicability and removal efficiency of eggshell technique as a low cost material for remediation abandoned mining sites under AMD hazard.



## 1. Introduction

The Çan lignite field basin, located in Çanakkale province at the north-western part of Turkey, has been operated to supply growing energy demands of Turkey for very long time. This basin was found in 1940 and operated until 1979 by private companies for heating purposes. The Çan lignite is now operated by Turkish Coal Enterprises (TKI) and the extracted lignite is mainly consumed in thermal power plant with 2 × 160 MW capacity for electricity generation. According to TKI (2002), the total reserves of Çan basin were estimated as 74 million tonnes and thus the mining activity in this region are expected to continue for many years. The Çan lignite basin consists of several small basins located in different places at the vicinity of Çan County, and some of them were previously operated by open-pit mining techniques without any precaution for its destructive influence on biological diversity. Actually, like many other worldwide mining activities, the environmental awareness was not considered as the first priority during and after mining activity and therefore the rehabilitation of abandoned mining sites was not common to prevent its adversely impact on human and wildlife.

The abandoned parts of Çan lignite basins and its vicinity, particularly basins found between Keciagili and Halilaga villages, have been known as an acid mine drainage (AMD) contaminated mining sites for fifty years due the oxidation of sulfur minerals found in geological sequences found in this region. Among these minerals, pyrite ($FeS_2$) was found as the most common mineral and its oxidation processes are given below equations:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \quad (1)$$

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \quad (2)$$

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

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (4)$$

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The AMD generation is a naturally occurring process produced from the oxidation of pyrite to sulfates and leading to the production of acidity, sulfate and iron whenever water containing oxygen comes into contact with sulfur present as sulfides in mineralized rock and mine wastes (Nriagu, 1978; Smith and Skema, 2001). The oxidation of such minerals release large amount of sulphuric acid, decrease the pH to below the 4.0, and finally increase the concentration of the dissoluble heavy metals such as Zn, Cu, Cd, As, Cr, Al, Mn, Ni, and Pb. The efficient heavy metal removal and neutralization of the AMD is virtually very difficult, expensive and time-consuming. According to Environmental Management Council of British Columbia (EMCBC 1996), its treatment costs millions of dollars and it can go on for many centuries to come with current technology. The damage restoration costs for USA was estimated by Feasby and Tremblay (1995) to be between 2 and 5 billion dollars, its world costs was estimated by Weatherell et al. (1997) as over 10 billion dollars, and currently in the USA the mining industries spends more than one million dollars each day in treatment of acid effluents (Grande et al., 2005).

Several approaches such as precipitation, chemical oxidation/reduction, ion exchange, solvent extraction, filtration, evaporation and membrane methods have been recommended and applied to neutralize AMD and remove dissolved heavy metals from contaminated aqueous systems until now. However, low-cost and high efficient techniques are alternatively investigated due to high cost of such kind of treatments. Liao et al. (2010) stated that the metal cation adsorption is quite promising due to its high efficiency, easy handling, availability of different adsorbents and cost effectiveness. Many researchers have recently applied numerous low cost natural materials (e.g., rice hulls and green algae, the shells of crab and shrimp, scoria, fly ash, zeolite, chitosan, sawdust, coal, sandstone, limestone, dolomite and waste eggshell) to treat heavy metals from aqueous solutions (Park et al., 2007; Zulfikar et al., 2012). In recent years, due to being produced globally from industries at large scale, some of these natural materials, particularly eggshell, may also be recognized as environmental waste products. The worldwide egg production was recorded as about 65 million tons in 2011 based on data provided from FAO (2014) and approximately 1.3% of this production was provided in Turkey. In addition widely availability of eggshell, Park et al. (2007) identified the calcined eggshell as a good material in the treatment of strong acidic water through a plausible uptake of heavy metal ions as well a good neutralization capacity. Despite containing these useful chemical components, egg shells have still not gained sufficient attention with regard to converting them from waste to reused materials (Oliveira et al., 2013).

Considering the porous inherent structure, widely availability and low cost sorbent characteristics of eggshell, a research program was initiated. The investigation acid mine drainage potential of abandoned mining sites located in vicinity of Çan County and understanding ability of eggshell for the neutralization of the AMD and removal of heavy metals of this abandoned mining site are main objectives of present study. For this purpose, waste water and solid samples were collected from acidic ponds and waste deposits to be used in laboratory experiments. Consequently, after all of testing and related analyses, the required amounts of eggshell were determined for acidic ponds found in this region for rehabilitation and management of this site.

## 2. Materials and methods

### 2.1. Field studies and sampling

The spatial distribution of ponds and spoil pile material was also defined and are given in Fig. 1. Based on field observation and pH measurements, it was found that there are four contaminated (acidic) and one uncontaminated ponds in this region. Heavy metals contaminated acidic water samples were collected from different locations at the shore of four ponds during spring season. To accurately determine dissolved metal concentrations, acidic water samples were taken at four different parts of each ponds and the average of these results were used for the purpose of this research. It is well known that the relative amount of constituents in ponds is changeable depending on evaporation and recharge rates, and so closed ponds are enriched in oxidation products during the low precipitation-high evaporation seasons. Considering this fact, in addition to the sampling during rainy season, one more waste water sample was also taken from Pond 1 in the dry season to determine seasonal changes in the heavy metal concentration of these ponds, and thus find the effect of evaporation on the level of pollution in this region. This sample was used for batch and column tests. Furthermore, samples were also extracted from lignite and spoil pile material to be used in column tests. The pH, electrical conductivity (Ec) and the total amount of dissolved solid in the water (TDS) were measured by using conventional pH meter and conductivity meter at field condition again at different representative locations.

### 2.2. Experimental program

#### 2.2.1. Static tests

Static tests were conducted in accordance to European standard (prEN 15875 2008) to get preliminary evaluation on ability of collected lignite and spoil samples to form AMD. For these tests, the percentages of sulfur (S) and carbon (C) were measured by using LECO devise in accordance with ASTM E1915-09 procedure. The total content of S and C were found as 0.60% and 1.98% for spoil materials, and 1.20% and 55.75% for lignite, respectively. The acid-generating potential (AP) is calculated from the percentage of S in samples and acid-neutralizing potential (NP) values were determined by performing acid-base titration. To perform this static test, eggshell, spoil materials and lignite samples were crushed to particle size of $-0.125$ mm. In order to measure NP of these samples, 2 g of dry powdered samples was added to 90 ml of distilled water and then a predetermined amount of 1 M HCl acid by considering mineralogical composition of samples was dropped to mixture. The mixtures were put on a magnetic stirrer for 24 h. The pH value of mixture was recorded after 22 h. According to European standard prEN 15875, the samples having a pH value below 2 should not be used for further steps of NP measurement. However, more HCl should be added to solution with a pH value higher than 2.5 until obtaining a pH value between 2 and 2.5. After eliminating not valid results, the solutions with a pH value between 2 and 2.5 after 24 h were titrated by 0.1 M NaOH to a pH of 8.3. The NP values of spoil materials, lignite and eggshell samples were determined by using the database consisting of the concentrations of HCl and NaOH, the volume added of HCl and NaOH and the dry mass of powdered samples. The NNP and NPR being expressed as function of AP and NP values were calculated for spoil materials, lignite and eggshell. These preliminary geochemical data are given in Table 1. This table reveals that the collected spoil material possesses a potential to generate AMD. When the acid-neutralizing potential and so the neutralization potential ratio of eggshell considered, it can be concluded that eggshell acts as a significant alkalinizing agent in connection with acidic water.

#### 2.2.2. Characterization of eggshell

The required amounts of eggshells were obtained from the wastes of homes, market, bakery and hatchery in Ankara, Turkey. In order to decrease its cost and so increase the applicability of eggshells as a potential treatment technique in practical