



Neutralisation of acid effluent from steel manufacturing industry and removal of metals using an integrated electric arc furnace dust slag/lime process

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Abstract

In this study, an integrated electric arc furnace (EAF) dust slag/lime ($\text{Ca}(\text{OH})_2$) treatment method was used to treat acid effluent generated by the same stainless steel producer. EAF slag alone was able to raise the pH to 8.7; thereafter, lime was added to increase the pH to the target pH of 12. The test proved that EAF dust slag, in conjunction with lime, can be used for neutralisation of acid effluent from a steel industry and for the removal of metals Co, Cr, Fe, Ni and Zn. The target metals were removed from the effluent, achieving greater than 99.6% removal. The process was simple and involves only mechanical mixing of the two constituents. Hence, it can be regarded as economically advantageous and environmental friendly since it only utilises a material considered as waste and a small quantity of lime. In addition to being a cost-effective replacement for expensive chemicals used in wastewater treatments, this method can alleviate the problem associated with the disposal of slag, a solid waste generated by a steel manufacturing industry.

Keywords Acidity · EAF slag · Effluent · Metal removal · Neutralisation · Treatment

1 Introduction

During the last century, a huge amount of industrial wastewater was discharged into rivers, lakes and coastal areas which can seep into the ground, introducing trace amount of industrial waste into water sources, seriously impacting the health of the eco-system and human life by polluting the aquatic environment [1–5]. In addition to becoming a major environmental concern, industrial wastewaters and acid mine drainages generated during various industrial and mining activities are impacting on water, one of the most important but rapidly dwindling natural resources [6, 7].

The wastewater from steel industries contains high levels of dissolved metals: nickel (to 4600 mg/L), total chromium (to 3500 mg/L), hexavalent chromium (to 200 mg/L), copper (to 170 mg/L) and lead (to 10 mg/L), and other wastes such as oil and grease (to 130 mg/L) and large

amount of sulphate can have pH values lower than 2.5 and acidity to the amount of 140,000 mg/L as CaCO_3 [8–10].

In the process of making steel in EAF, fluxes are added into the furnace along with the scrap metal to remove unwanted substances by generating a slag which is a mixture of the impurities [11–13]. At a scrap steel recycling plant, in addition to wastewater an average of 600-kg solid by-products, namely slag, dust, mill scale and sludge, are produced per ton of steel produced [11]. Of all types of solid wastes generated in the EAF, slag is the most significant in quantity, for its amount ranges from 60 to 263 kg per ton of raw steel produced based on the furnace operating method and the characteristics of the raw materials [14, 15].

The type of EAF slag, commonly known as dust slag, is one of the critical and hazardous wastes encountered in the EAF steelmaking industries [16]. It is produced when the volatile components are fumed off and collected with

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particulate matter in the off-gas cleaning system during the steelmaking process [17–19]. Generally, EAF process generates 10 kg of EAF dust per ton of steel produced; however, the range varies from 5 to 30 kg per ton of steel produced, depending on factors such as the furnace characteristics and the quality of the scarp [20, 21].

In recent years, considerable attention has been paid to industrial wastes discharged to land and surface water [22]. As concern about metal contaminants in water increases, regulations governing the discharge of wastewater have become more stringent and treatment works have set lower discharge limits of metals [23, 24]. The increase in environmental awareness, the practice of sound environmental management demanded by stringent regulations over the past decades and the need for low-cost treatment method have led to serious investigations to develop viable methods [25, 26].

According to several studies, chemical precipitation of chromium, cobalt, nickel and zinc can be achieved by raising the pH to between 9 and 10.5, where the metals are transformed into their respective highly insoluble hydroxides [27–31]. Techniques using chemical precipitation employed currently by most metal finishing businesses are time-consuming and require extensive equipment and handling [32].

High operational costs associated with chemicals and the treatment processes as well as increasingly stringent environmental regulations have forced industries to find cost-effective and efficient effluent treatment methods and materials with properties similar to the conventional alkaline materials used in the neutralisation processes [33, 34]. As a result, in recent years there has been increasing interest in the research on waste materials and by-products, with possible application in wastewater treatment processes [35].

Since pH is the major factor in neutralisation and metal removal from acid effluents through precipitation, the aim of this research was to find a cheaper but effective alternative material which could raise the pH to the required level. The candidate material selected for this study was EAF dust slag. Its major components are basic oxides including CaO (35.4%), FeO/Fe₂O₃ (19.2%), MgO (7.8%) and Al₂O₃ (6.9%) rendering its leachate alkaline [36, 37]. This property can be exploited to utilise the slag for neutralisation and the removal of metals from acid effluent of industries by integrating it with lime.

The purpose of this study was to find out if an integrated process involving EAF dust slag and lime can be applied to neutralise and to remove metals from metal-laden acid effluent generated by a steel industry. It was also intended to develop a treatment method that can result in environmentally benign water through a more sustainable, cost-effective treatment method taking

environmental, economic and health impacts into consideration. The study investigated if a slag, a by-product generated during steel production, can be used as an alternative for the treatment of wastewater than being disposed off in landfills causing damage to the environment and incurring levy cost to the companies.

The objectives of the study were:

- To determine if dust slag, the by-product generated by EAF during steel production, can be applied to neutralise acid effluent generated by a steel industry
- To determine the optimum condition to remove the acidity from the effluent
- To determine if iron can be removed from acid effluent by using only the dust slag
- To find out if the dust slag can be used to remove Cr, Co, Ni and Zn in conjunction with lime

2 Materials and methods

2.1 Feedstock

All the chemicals used in this experiment were of analytical grade and used without any further purification. The HCl was obtained from SMM chemicals supplier. The NaOH was bought from Ace Chemical suppliers, and the Ca(OH)₂ was procured from Sigma.

Acid steel industry effluent and EAF dust slag were collected from the stainless steel industry that uses scrap metal as raw material to produce steel.

2.2 Equipment

Knick pH meter 766 Calimatic (Germany) was used to measure pH throughout the process. The rod stirrer used for the agitation was IKARW 20 digital stirrer (Germany). ICP-OES (Spectro Arcos, Arcos-FHS, Germany) was used for the determination of metal content.

2.3 Procedure

Prior to treatment with the slag, the wastewater was scanned for metal content and it was found to contain Fe, Mg, Ca, Na, K, Mn, Al, Cr, Co, Ni, Zn, Cu and Ba in different concentrations. The target elements for the study were Fe, Cr, Co, Ni and Zn. The study was carried out using 1-L plastic beaker and road stirrer. Based on the amount of alkali content in the slag and the acidity of the effluent, the amount of the slag required for effective neutralisation was calculated using an alkalinity-to-acidity ratio of 3:2. All the analyses were carried out in triplicate.

One litre of effluent was measured into a beaker, and the calculated amount of slag was added into the container. The contents were stirred continuously at 380 rpm using rod stirrers. Samples were collected at intervals of 10 and 30 min as well as 1, 2, 4, 24, 48 and 96 h from the sample for the determination of pH, acidity and metal content. The content was made up of its original 1 L volume after each sampling. After 96 h, the process was continued by adding pure lime (Ca(OH)_2) and two more samples were collected at pH 9.5 and pH 12.

The collected samples were filtered immediately through Whatman No. 1 filter paper. pH and acidity were analysed using the method given below. Metal content was determined using ICP-OES (Spectro Arcos, Arcos-FHS, Germany).

2.4 Analytical

The slag was dried in an oven for 2 h at 105 °C, crushed to powder after cooling and sieved through a 300- μm -pore-size sieve. The amount of free lime and total alkali in the slag were determined as follows.

The amount of free lime was determined as Ca(OH)_2 using the following method. 0.25 g of the dried crushed and sieved slag sample was weighed into a beaker, and 250 ml of deionised water was added and stirred for 15 min. The solution was filtered through Whatman No. 1 filter paper. Fifty millilitres of the filtrate was titrated against standard 0.1 N HCl to pH 7. The free lime content was calculated from the mass and volumes using the formula given in Eq. 1:

$$\% \text{Ca(OH)}_2 = \frac{37 * C * V1 * V2}{1000 * V3 * M} * 100, \quad (1)$$

where C is the concentration of HCl, $V1$ the volume of HCl used in the titration, $V2$ the total volume of the sample, $V3$ the volume of the sample titrated and M the mass of the slag.

Total alkali in the slag was determined as CaCO_3 by using the following method. 2.5 g of the dried, crushed and sieved slag was weighed into a beaker; 100 ml of 1 N HCl was added and boiled for 2 min. The solution was cooled to room temperature, made up to the mark of 100 ml with DI water and filtered through Whatman No. 1 filter paper. Forty millilitres of the filtrate was titrated with 1 N NaOH to pH 7.

The total alkali content as CaCO_3 was calculated from the mass and volumes using the formula given in Eq. 2:

$$\% \text{CaCO}_3 = \frac{50 * C1 * V1 - C2 * V2}{1000} * \frac{M * V3}{V4} * 100, \quad (2)$$

where $C1$ is the concentration of HCl, $V1$ the volume of HCl, $C2$ the concentration of NaOH, $V2$ the volume of NaOH, $V3$ the volume of the solution titrated, $V4$ the total volume of the sample solution and M the mass of the slag weighed.

Acidity and pH of the raw effluent as well as all the samples taken during the process were also determined. pH was determined by using a pH probe directly, whereas acidity was determined as follows [38].

Five millilitres of the filtered sample (filtered through Whatman No. 1 filter paper) was diluted by adding 45 ml deionised water. The solution was titrated with 0.1 N NaOH to pH 8.3. Acidity was calculated from the volumes using the formula given in Eq. 3:

$$\text{Acidity} \left(\frac{\text{g}}{\text{L}} \text{ as } \text{CaCO}_3 \right) = \frac{50 * C * V1 * 100}{V2}, \quad (3)$$

where C is the concentration of NaOH, $V1$ the volume of NaOH and $V2$ the volume of the sample titrated.

3 Results and discussion

The pH of the raw effluent measured using pH meter was 0.64, while the acidity determined using the above method was 36 g/L as CaCO_3 .

3.1 Free lime and total alkali content

Free lime content, which is the water-soluble alkali, and the total alkali content, that is capable of reacting with the acid in the effluent, in the slag determined using the methods above are given in Table 1.

3.2 Effect of operating time on acidity

Since acid is used extensively in pickling during steel production, effluent from a stainless steel industry is highly acidic and rich in various metals [39]. Currently, lime is used predominantly for neutralisation and the removal of metals. The outcome of this study indicated that EAF dust slag can be used as a replacement for lime to neutralise and remove acidity from iron and steel industry effluent. It effectively raised the pH to an environmentally acceptable range in the presence of very high iron content. The

Table 1 Free lime and total alkali in the slag

Parameter	Sample mass(g)	%
Free lime	0.25	3.6 ^a
Total alkali	2.50	92.4 ^b

^a Ca(OH)_2

^b CaCO_3

Table 2 pH and acidity change with respect to time

Time	0 ^a	10 ^a	30 ^a	1 ^b	2 ^b	4 ^b	24 ^b	48 ^b	72 ^b	96 ^b
pH	0.64	3.0	3.1	3.1	2.9	3.1	8.1	8.2	8.5	8.7
Acidity (g/L)	36 ^c	11 ^c	8 ^c	4 ^c	2.7 ^c	0.8 ^c	ND	ND	ND	ND

ND not detected

^aMinutes

^bHours

^cg/L

pH of the raw effluent, which was 0.64, was raised to 8.1 after stirring the mixture for 24 h. After adding the slag, the mixture was stirred at 380 rpm. The pH increased rapidly to 3.0 in 10 min. This fast change in pH was due to the presence of water-soluble free lime in the slag. However, the pH increase slowed down once all the free lime was consumed and reached 8.1 after 24 h, resulting in complete neutralisation, indicating that the alkali in the slag has reacted with the acid in the effluent. It was raised further to 8.2 after 48 h of agitation and to 8.7 after 96 h, which is well in the acceptable range of 6–9 to discharge wastewater effluents into receiving water bodies with respect to acidity [40].

Dust slag is alkaline by nature due to the hydrolysis of the basic oxide components such as CaO as described by Eq. (4), giving it an excellent neutralising potential [41]:



The acidity of the raw effluent was measured and found to be 36 g/L as CaCO₃. After 24 h of stirring, no acidity was detected. Table 2 shows that 89% of the acidity was removed within 60 min and 98% after 4 h. The change in pH and acidity was measured at time intervals throughout the experiment, and the results are given in Table 2.

3.3 Removal of iron

The method has proven to be effective to remove iron from an iron and steel industry acidic effluent containing a very high amount of iron and other metals using only the dust slag. The Fe²⁺ in the effluent was oxidised to Fe³⁺ and reacted with the OH⁻ ions generated from the hydrolysis of the basic oxides in the slag to form an insoluble Fe(OH)₃, removing the iron from the effluent in the form of precipitate. Total iron content in the raw effluent was 4692 mg/L. No iron was detected after 24 h of stirring using only slag. The result is shown in Fig. 1.

3.4 Removal of other metals

Integrated EAF dust slag/lime method proved that it can be used for the removal of metals from the steel industry

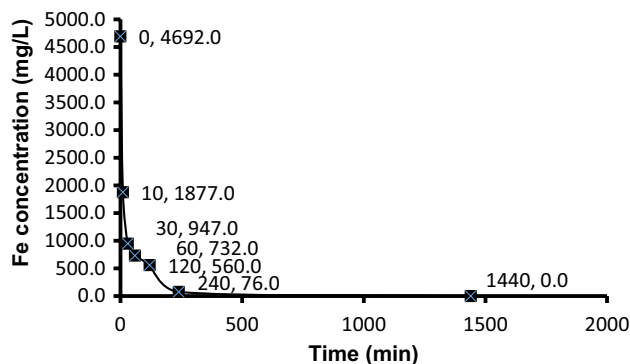


Fig. 1 Effect of time on Fe concentration

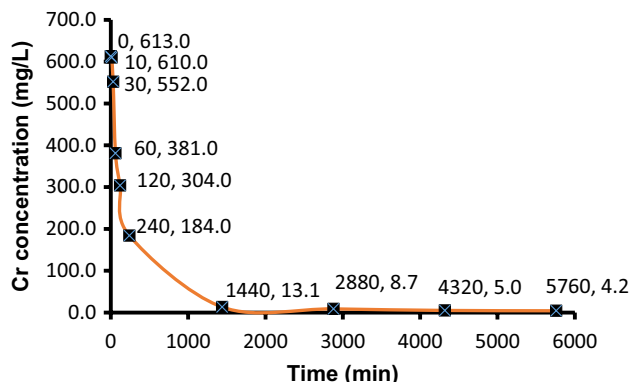


Fig. 2 Effect of time on Cr concentration

acid effluent with a highly reduced cost. Metals Cr, Fe, Co, Ni and Zn form insoluble hydroxides at higher pH, removing them from the effluent. The concentration of the metals investigated in the raw effluent varied from 613 mg/L (Cr) to 24.4 mg/L (Zn). After the treatment, the concentration of the four metals decreased, achieving removal of 96.2% (nickel) and 96% (cobalt), while Cr and Zn were removed almost completely (> 99%). The amount of slag added was 54 g/L, and the amount of lime added was 0.7 g/L. The pattern of the reduction in the concentration of the metals with respect to pH is shown in Figs. 2, 3, 4 and 5.

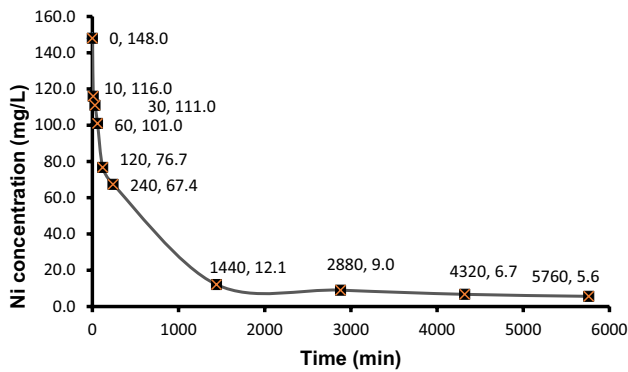


Fig. 3 Effect of time on Ni concentration

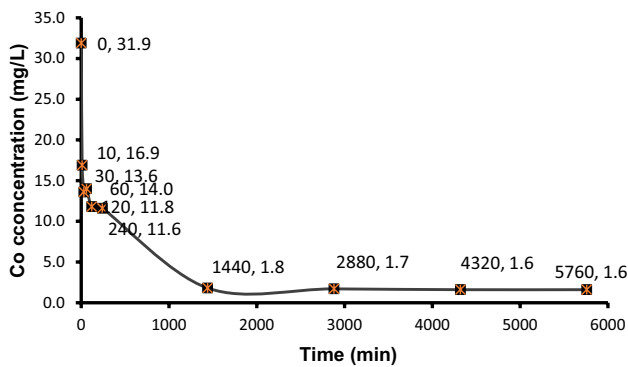


Fig. 4 Effect of time on Co concentration

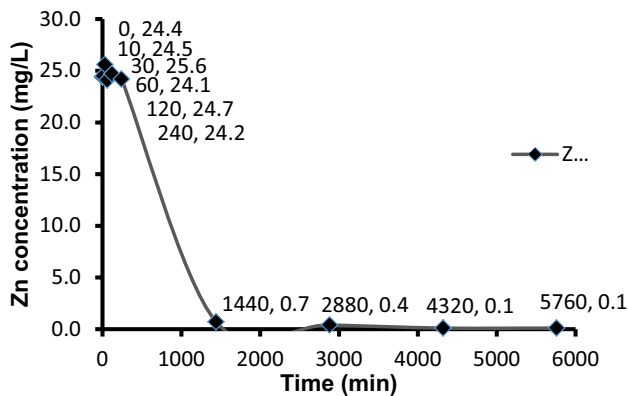


Fig. 5 Effect of time on Zn concentration

After 96 h (5760 min), the process was continued by adding pure lime ($\text{Ca}(\text{OH})_2$) and samples were collected at pH 9.5 and 12. The concentration of Cr dropped from 4.2 mg/L to 0.5 mg/L at pH 9.5 and ND at 12; Ni dropped from 0.9 mg/L at pH 9.5 to 0.4 mg/L at pH 12; Co dropped from 1.6 mg/L to 1.5 mg/L at pH 9.5 and to 1.1 mg/L at

pH 12; Zn which was 0.1 mg/L was ND at both pH 9.5 and pH 12.

4 Conclusion

The study demonstrated that EAF dust slag can be used for neutralisation of acid effluent from steel industries. Acidity was removed completely in 24 h. The slag alone was capable of neutralising the highly acidic effluent effectively raising the pH to greater than 8 in 24 h. The study also demonstrated that the EAF dust slag alone can remove iron completely from the wastewater achieving a 100% removal in 24 h. The concentration of the other metals was also reduced considerably using the slag only, resulting in the removal of Zn (99.6%), Cr (99.3%), Ni (96.2%) and Co (95.0%). Though this was considered to be effective with regards to the five metals, a small amount (0.7 g/L) of lime ($\text{Ca}(\text{OH})_2$) was added to ensure more removal of the metals, resulting in a better percentage of removal.

Slag itself is a waste product and causes problems of disposal for the steel industries. Removing it to be disposed off in landfills has cost implications for the industries since a large levy is paid for its disposal. Using it for neutralisation also saves this cost.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Ethical approval The authors declare that there is no ethical issue with the research. It does not involve any living things and release or contact with the surrounding environment.

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