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Application of fly ash in the agglomeration of reactive mine tailings

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Abstract

Agglomeration is one of the most effective methods of dealing with reactive mine tailings in the prevention of acid mine drainage. The agglomeration process, accomplished with the use of a conventional binder such as Portland cement, immobilizes the reactive components of the mine tailings and results in the formation of strong pellets which remain impervious to weathering and leaching. The objective of this study was to evaluate the fly ash as a binder, either by itself or in combination with cement, in the mitigation of acid mine drainage caused by the reactive tailings. Two different acid mine tailings samples differing in their reactivities were chosen. These tailings were obtained from Noranda, Quebec, Canada and Cyprus Thompson Creek, Clayton, Idaho. The fly ash was obtained from Mineral Specialities Inc., Billings, Montana. Agglomeration tests were performed with fly ash and Portland cement. The crushing strength and the leachability of the cured agglomerates were evaluated. Preliminary results indicate that the use of fly ash significantly reduces the requirement of cement without any decrease in strength and immobilization effect. In fact, it was shown that the fly ash improved crushing strength of the agglomerates. This increase was substantial in the case of reactive tailings (Noranda). The leaching (simulated TCLP) tests performed on the Noranda Tailings agglomerates prepared using fly ash/cement resulted in the much lower level of extractable ions concentration and well below the regulatory level than from the agglomerates prepared using either fly ash or cement alone.

Keywords: Agglomeration; Crushing strength; Fly ash; Mine tailings; Leaching; Mine drainage

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1. Introduction

Fly ash is a waste product generated from the combustion of fossil fuels in industrial operations such as power generation, oil refining and cement manufacturing. It is present in flue gases collected by air pollution control devises, such as electrostatic precipitators. Fly ash particles mainly consist of silica and alumina. Other components may include carbon, phosphorus, sulfur, alkali compounds, and oxides of calcium, iron, magnesium, potassium, sodium, titanium and vanadium. Fly ash is currently being used in the cement and concrete industry as a raw material and as an additive as well as a substituent for cement in the final mix of lightweight aggregates [1].

Acid mine drainage is one of the serious environmental concerns facing the mining and mineral processing industries. This problem is particularly acute with the sulfide ores which are generated in the mineral dressing operations [2–5]. Oxidation of these minerals in the ambient air and their reactions by certain microorganisms produces sulfuric acid which solubilizes the heavy metals. The acid, as well as the heavy metals, permeates through the ground and contaminates ground water, rivers and streams. Acid mine drainage can, however, be controlled in several ways. These include neutralization [6], chemical precipitation [7,8], application of bactericide [9–11] and agglomeration [12]. Chemical precipitation is one of most commonly used pump and treat approach for liquid streams [13,14]. Agglomeration, on the other hand, is a pollution prevention approach in which the tailings (solid invaluable by-product stream of a mineral beneficiation plant) are immobilized in an agglomerate (i.e. pellet or briquette) form, thus avoiding acid formation and subsequent leaching of the heavy metals. Agglomeration of tailings is accomplished with the use of a binder such as cement to increase the strength of the agglomerates. In this study, fly ash was used as a binder in combination with Portland cement in the agglomeration of two different tailings. The effectiveness of fly ash as a binder was evaluated by crushing strength tests performed on the cured agglomerates. The immobilization of the reactive components of the tailings was also determined by conducting leaching tests (simulated TCLP tests) on the cured agglomerates.

2. Experimental

2.1. Materials

Tailings used in this study were obtained from the Noranda Mines, Quebec, Canada, and Cyprus Thompson Creek (CTC), Clayton, Idaho. These samples differed in their chemical composition and in their reactivities. Fly ash was obtained from Mineral Specialities Inc., Billings, Montana. Portland cement was obtained from Basalite, Inc. Carson City, Nevada. The mineralogical and elemental composition of these materials reported in this study was provided by the respective supplier.

2.2. Pelletizer

Tailings samples were agglomerated in a laboratory built disc pelletizer of 40.5 cm diameter and 9 cm depth. The dewatered plant tailings were premixed with fly ash and/or Portland cement with a sufficient amount of water and transferred to the pelletizer. The disc pelletizer settings were kept constant in all the runs at the following values: pelletization time 30 min, speed of the disc pelletizer 30 rpm, and inclined angle of the pelletizer was kept at 30°. The moisture content of the mixture during the agglomeration was controlled with frequent spraying of water, which was in the range 15–20% (by weight). At the end of agglomeration, the agglomerates were transferred to a plastic container and cured for a period exceeding 15 days at room temperature with intermittent water spray.

2.3. *Crushing strength tests*

The crushing strength of the cured agglomerates was evaluated by a simple method [15]. Individual agglomerates are placed between two parallel plates and loaded with a uniformly increasing force until failure occurs. This was reported as Newtons per pellet for an average pellet size of 13 mm diameter.

2.4. *Leaching tests*

The leaching propensities of the as-received tailings, fly ash and cured agglomerates were determined in a well stirred leaching vessel. This procedure was different from the conventional TCLP and EP extraction tests [16]. It is well known that these procedures are carried out for hazardous wastes containing toxic metals and volatile organics. Since the tailings used in this study contained no organics and very low levels of hazardous and toxic metals, problems related to TCLP tests such as cleaning of ZHE vessel, methods to collect samples from ZHE vessel etc. were circumvented by adopting a simple leaching procedure [12]. Moreover, this leaching procedure provides conditions similar to the weathering conditions that these agglomerates are often subjected to in the environment. In the leaching procedure used in this study, approximately 100 g sample was placed in 200 ml of tap water and was allowed to stand for 15 days. This time is several order of magnitudes higher than 18 h used in a conventional TCLP test. At the end of 15 days, the weight of the sample was measured and the leachate was analyzed for the metals in solution by an ICP (inductively coupled plasma spectrophotometer). The reduction in the weight of the agglomerate was related to the integrity of the agglomerates whereas the concentration of the metals in solution was related to the stability of the agglomerates.

3. Results and discussion

3.1. *Characterization of the tailings and binders*

Size distributions of the tailings are considered to be important in the determination of their reactivities. Finer size tailings, by virtue of their higher surface area, tend to be more highly reactive towards oxidation, both by ambient air and microorganisms. Similarly, in the case of fly ash, the finer size particles are expected to integrate with the tailings and function more effectively. A nominal comparison could be made by comparing their median size (e.g. d_{50} or 50% passing size). In order to determine their respective median size, the cumulative particle size distributions of the two tailings samples and the fly ash are plotted in Fig. 1. These distributions were determined by wet sieving procedure. Results show that the fly ash is a very fine material in that as much as 80% or more was found to be finer than 38 μ. The scanning electron microscopic analysis of the fly ash furthermore indicated that majority of the particles were in the 1 fm size range. As indicated in Fig. 1, the amount of material passing 38 μ size in the case of the Noranda tailings and the CTC tailings was only 45% and 30%, respectively. The median size for the Noranda tailings and the CTC tailings was estimated to be around 45 and 70 μ, respectively. The Blain fineness of the cement was 3200 $cm^2 g^{-1}$ [17], therefore, particle size was not determined.

The chemical analyses of the Noranda and CTC tailings provided by the supplier are presented in Table 1. It must be emphasized that, although the method of analysis represents the chemical composition of tailings in terms of the oxides, the samples need not necessarily contain the stated oxides, and sometimes an oxide for a given element may be totally absent. However, relative amounts of the other elements determined are reliable in such analysis. The analysis indicates a significant difference between the two samples in terms of the iron content, which makes the Noranda tailings more reactive. Another important constituent which determines the reactivity of the tailings is the sulfur

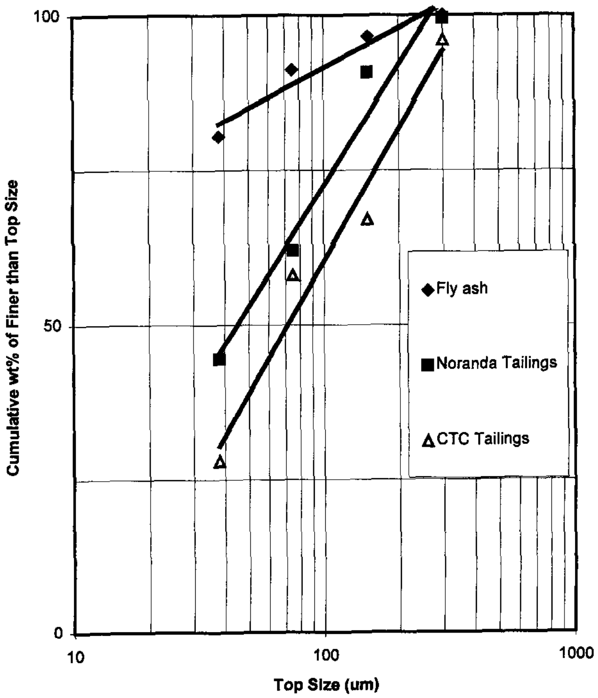


Fig. 1. The cumulative particle size distribution of two tailings and fly ash.

Table 1
Mineralogical composition of the CTC and Noranda tailings

Oxides/element	Composition (wt.%)	
	CTC tailings	Noranda tailings
SiO_2	64.36	79.08
Al_2O_3	12.86	2.6
Fe_2O_3	1.82	4.33
MgO	0.36	0.854
CaO	1.01	0.69
Na_2O	9.56	1.47
K_2O	3.02	0.34
S	3.0	8.5

content. Note that the CTC sample contains 3.0% sulfur, whereas the Noranda tailings contain 8.5% sulfur. Based on the particle size consideration and the chemical composition, the Noranda tailings are clearly more reactive than the CTC tailings. The higher amount of residual iron and sulfur containing tailings are susceptible to cause acid mine drainage in the presence of air, water and certain bacteria to yield large quantities of iron, sulfate and acidity as indicated in the following thermodynamically favorable chemical reactions [12]:

$$FeS_2 + 7/2O_2 + H_2O \Rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad \Delta G^0 = -280.928\,\mathrm{kcal\,mol^{-1}}$$

$$4Fe^{2+} + O_2 + 4H^+ \Rightarrow 4Fe^{3+} + 2H_2O \quad \Delta G^0 = -43.278\,\mathrm{kcal\,mol^{-1}}$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \Rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$

$$\Delta G^0 = -129.455\,\mathrm{kcal\,mol^{-1}}$$

The chemical composition of the fly ash and the Portland cement provided by the suppliers are given in Table 2. The reactive mine tailings consists of potentially acid forming minerals and tend to react with alkaline materials contained in the fly ash thereby effectively forming the environmentally benign neutral compounds which are resistant to weathering and chemical environment.

The effectiveness of fly ash as a binder depends on its alkalinity equivalent which is

Table 2
Mineralogical composition of the fly ash and Portland cement [17]

Oxides	Composition (wt%)	
	Fly ash	Portland cement
SiO_2	37.95	22.1
Al_2O_3	17.17	3.9
Fe_2O_3	7.09	3.5
Lime	13.50	65.4
MgO	4.21	1.1
SO_3	14.92	2.6

indicated by the amount of calcium oxide present in the sample. The analysis of fly ash, as presented in Table 2, shows that it contains 13.5 wt.% of calcium oxide which further increases the alkalinity of the agglomeration process, reducing the curing time to achieve a targeted crushing strength level.

3.2. Effect of fly ash

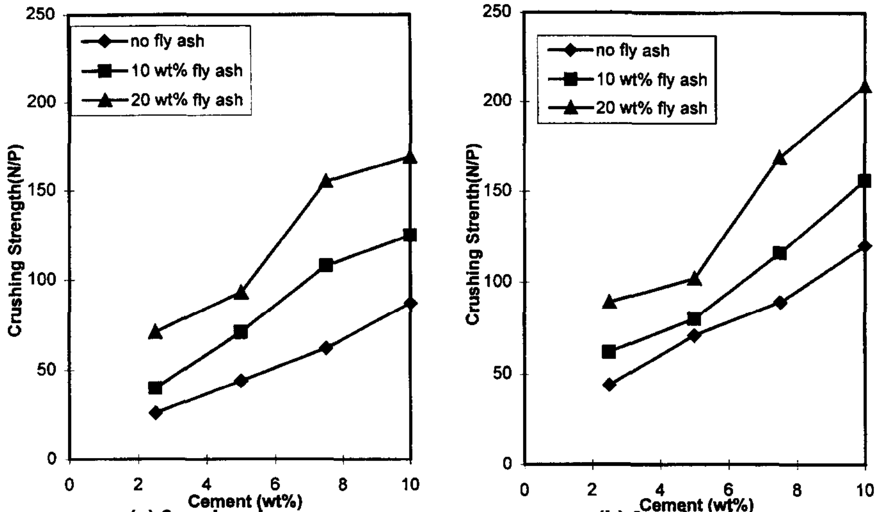
3.2.1. Crushing strength

Agglomeration of both the tailings with fly ash alone was not observed to be as successful as with cement [12]. Although stable agglomerates were formed, the binding strength was less than desirable. Even a long curing period of 15 days did not improve the strength of the agglomerates, which crumbled when dropped from a height of 1.3 m. This observation remained consistent, even when the fly ash content in the agglomerates was increased from 5 to 20% by weight. The use of fly ash alone was found to be an inadequate proposition for the agglomeration of tailings.

The fly ash was, subsequently, used as an additive in combination with Portland cement to observe whether it augments the performance of Portland cement. Portland cement was shown to be an effective binder for the same two tailings in a different study [12]. Fly ash and cement were used in several combinations, and the crushing strengths of the resulting agglomerates from both the tailings were evaluated. The change in crushing strength of the CTC agglomerates containing different Portland cement levels is shown in Fig. 2(a)–(d) as a function of fly ash dosage and curing time. For a given curing period, higher Portland cement and higher fly ash content result in higher crushing strength. In each of the Fig. 2(a)–(d), the crushing strength of agglomerates, obtained using cement alone as a binder (at levels 2.5, 5, 7.5 and 10%), was compared with that using a combination of binders consisting of the same amount of cement in addition to 10 and 20% fly ash. It is apparent from Fig. 2(a)–(d) that in each case the crushing strength significantly increased with the addition of fly ash. Although the observed increase in the strength of agglomerates was not linear, the higher crushing strength was always noted with those containing higher amounts of fly ash. The results also indicate that crushing strength was increased during the first 6 days of curing and further enhancement was noted to be marginal in the following 9 days curing period. In general, the strength enhancement of the agglomerates as a function of fly ash content appeared to be unrelated to the amount of the cement used in the mixture since the net increase was nearly equal in all cases viz., 2.5, 5, 7.5 and 10% cement (Fig. 2(a)–(d)). These results clearly indicate that, although fly ash, being a waste product, cannot function as a stand alone binder for the agglomeration of mine tailings, it can however be used in combination with cement to obtain agglomerates of adequate strength.

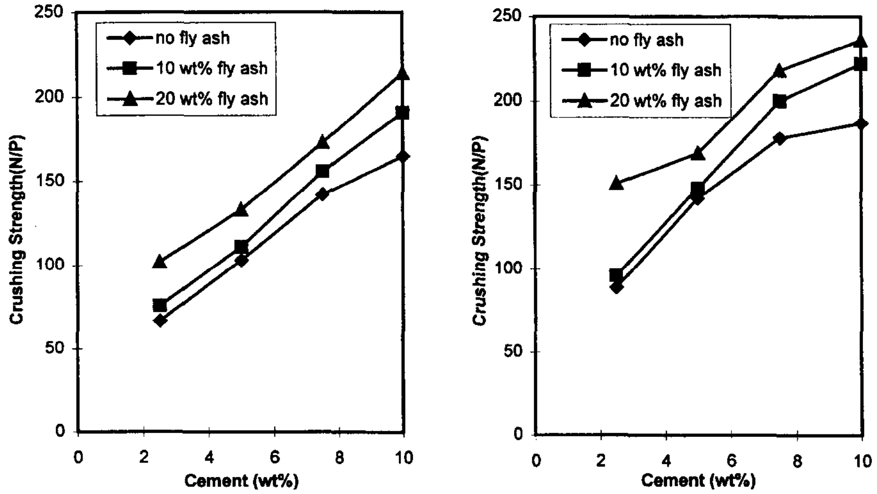
Fig. 3 shows the effect of curing time on CTC agglomerates prepared with 5% cement and at different levels of fly ash. Note that higher dosages of fly ash help to reach a given crushing strength with much reduced curing time. Also, for a given curing time, the agglomerates prepared using higher dosage of fly ash result in a higher crushing strength. It is clear from Fig. 3 that the increase in the curing time from 3 to 15 days results in an average increase of the crushing strength from 75 to 150 NP.

Similar crushing strength results obtained with the Noranda tailings agglomerates are



(a) 3 curing days

(b) 6 curing days



(c) 10 curing days

(d) 15 curing days

Fig. 2. Effect of fly ash on crushing strength of CTC agglomerates (crushing strength as a function of wt.% of cement).

presented in Fig. 4(a)–(d). In the agglomeration of these tailings, combination of 20% fly ash with 2.5, 5 and 10% cement was used. It is evident from Fig. 4(a)–(d) that the addition of fly ash has again significantly increased the crushing strength of the agglomerates. However, there are two important differences to be noted in the case of the Noranda tailings. Firstly, the increase in crushing strength for Noranda tailings due to fly ash addition is relatively large in comparison to that observed in the case of CTC tailings. Secondly, the strength of the Noranda agglomerates was observed to increase with the increase in curing period, mostly after 6 days. This was expected because of the

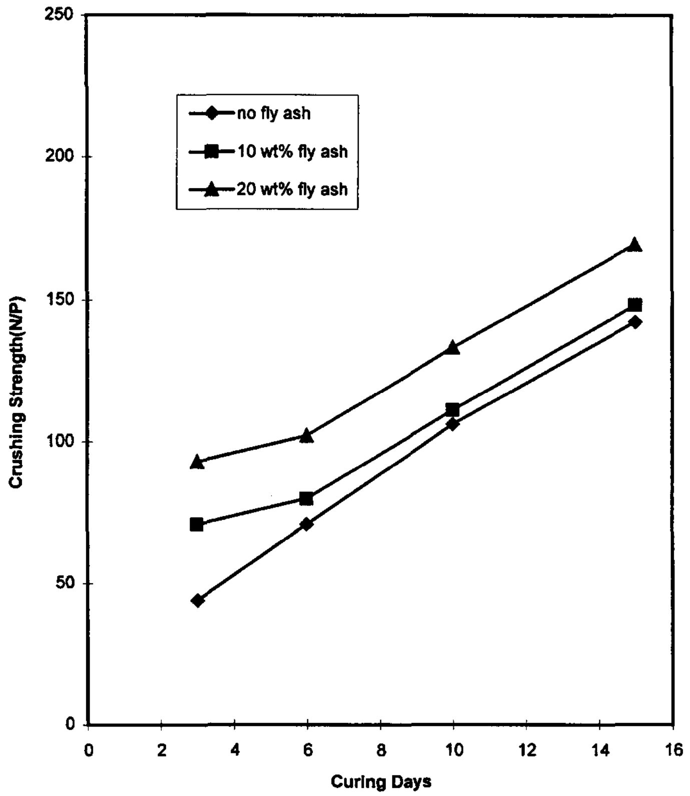
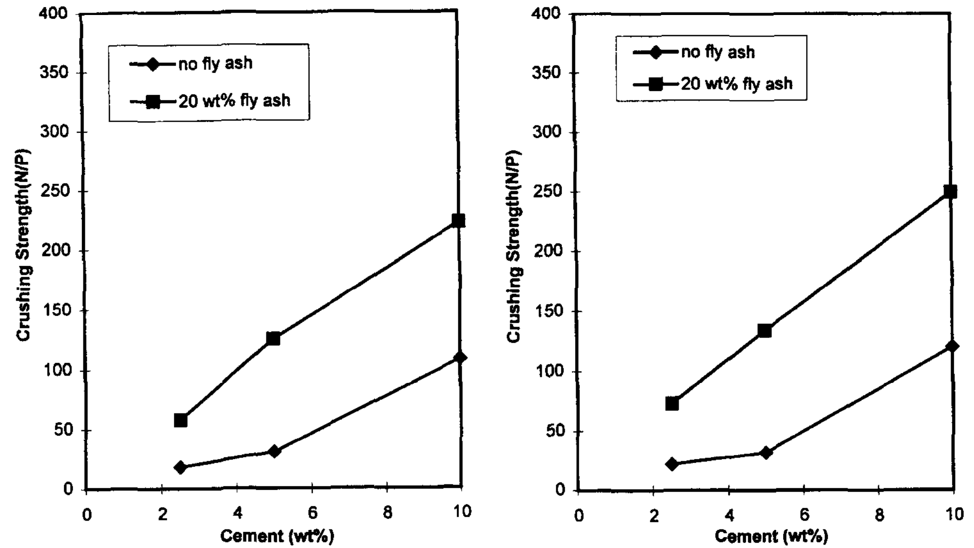


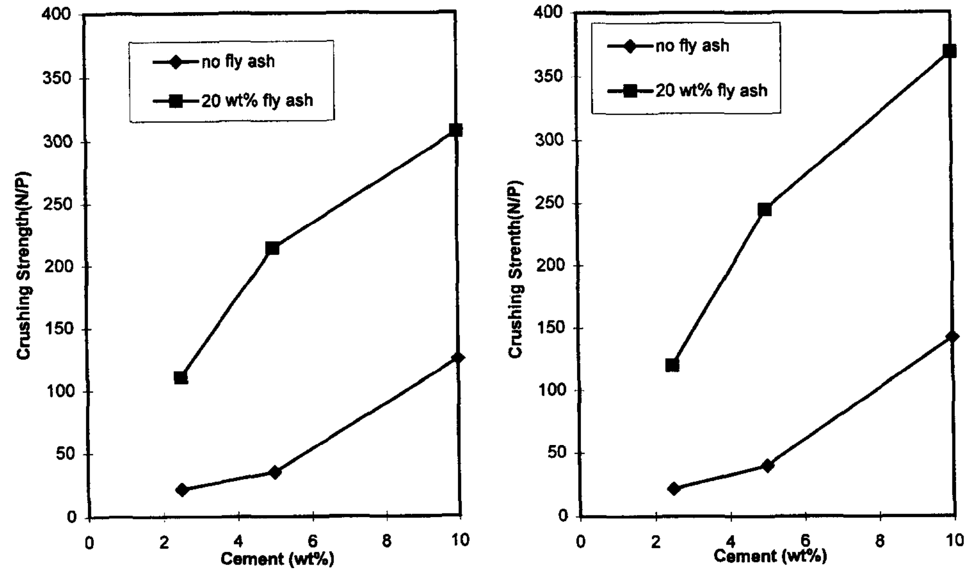
Fig. 3. Effect of fly ash on crushing strength of CTC agglomerates with 5 wt.% cement.

high acidity of the tailings. Fig. 5 shows the effect of curing time on the Noranda Tailings agglomerates prepared with 5% cement. Again, with the addition of fly ash, by increasing the curing time from 6 to 15 days, the crushing strength was increased from 125 to 250 NP. Note that when agglomerates are formed with no fly ash, curing time has no effect on the crushing strength. In the case of Noranda tailings, crushing strength increase observed in the case of binders consisting of 20% fly ash in combination with 5 and 10% cement was very substantial and resulted in an increase of 500 and 300%, respectively, based on the value obtained with cement alone. This indicates that a significant increase in strength can be achieved by using an intermediate combination of binders (i.e. 5% cement and 20% fly ash).

The synergistic effect of the fly ash was thus found when used with cement in the agglomeration of Noranda tailings which are comparably more reactive than CTC tailings. This can be explained as follows: essentially, binders are alkaline materials and have a tendency to react with the acid forming minerals in tailings. These reactions result in the formation of neutral chemical compounds which coat the minerals, thereby providing immobilization of reactive minerals in the tailings and prevent further oxidation either by ambient air or by microorganisms. The reactive components in CTC tailings, such as sulfides, are relatively lower in comparison to the Noranda tailings.



(a) 3 curing days (b) 6 curing days



(c) 10 Curing days (d) 15 curing days

Fig. 4. Effect of fly ash on crushing strength of Noranda agglomerates (crushing strength as a function of wt.% of cement).

Thus, the time required by the sulfide minerals in the CTC tailings to react with the alkaline materials in the binders is comparably short. This is consistent and as observed in Fig. 4(a)–(d), in the case of CTC tailings where the enhancement in the crushing strength reaches relatively quickly. Conversely, in the case of Noranda tailings the reactive minerals are in greater abundance and the agglomerates require a longer time

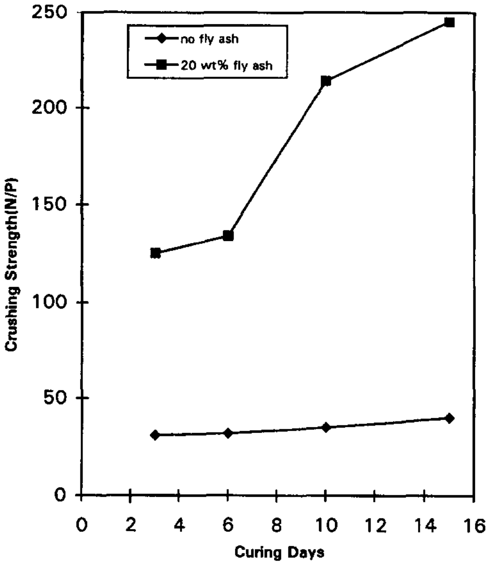


Fig. 5. Effect of fly ash on crushing strength of Noranda agglomerates with 5 wt.% cement.

for the neutralization reactions to take place and thereby attain greater crushing strength values. The results presented thus far indicate that fly ash is very effective for the reactive tailings in imparting strength to the agglomerates. However, the mechanism of synergistic interaction between the cement and fly ash in increasing the strength of the agglomerates can only be attributed to the added alkalinity of the cement provided by the presence of lime in the fly ash.

3.2.2. Leaching characteristics

In order to determine the effectiveness of the agglomeration process, the agglomerates obtained from the Noranda tailings were subjected to a leaching test. In these tests the leaching propensity of the agglomerates was compared to that of as-received tailings. The leaching tests under identical conditions were conducted for a period of 15 days, i.e. a time period far exceeding that of 18 h used in the TCLP test. At the end of this period pH, weight loss and the presence of dissolved ions in the leachate were determined. The results are presented in Table 3. As seen from the table, the immobilization effect measured in terms of the dissolution of heavy metals from the agglomerates is remarkable when fly ash is used in combination with cement. Note that, the level of dissolved metal ions from the agglomerates prepared with fly ash and cement is below the regulatory levels. On the other hand, when the fly ash and the Portland cement are used individually, then the immobilization effect is not substantial. This is clear because the leaching tests performed on the agglomerates prepared under these conditions don't meet the EPA regulatory levels [18]. The presence of large amounts of calcium is attributed to the alkalinity of the fly ash and cement. It has been reported that leaching of the agglomerates further enhances the crushing strength by as much as 35% due to the extensive surface precipitation on the agglomerates. The precipitates were believed

Table 3

Concentration of dissolved metal ions (in ppm) resulting from 15 days leaching tests conducted on as-received Noranda tailings, agglomerates prepared with 20% fly ash, agglomerates prepared with 20% fly ash + 5% Portland cement and agglomerates prepared with 20% Portland cement

	As-received Noranda tailing	EPA regulatory levels [a]	Agglomerate 20 wt.% fly ash + no cement	Agglomerate 20 wt.% fly ash + 5 wt.% cement	Agglomerate 20 wt.% cement + no fly ash
Final pH	3.3	6.5–8.5	10.3	7.9	10.8
Weight loss (%)	100	NA	4.7	0.2	10.0
Zn	238.7	5.0	0.1	< 0.1	1.2
Cd	1.1	0.005	< 0.1	< 0.05	0.6
Pb	1.3	0.015	0.4	< 0.1	0.5
Cu	3.2	1.3	1.9	0.1	2.5
Co	3.2	–	0.1	0.1	< 2.0
Ni	2.5	0.1	0.6	< 0.1	0.8
Fe	917.7	0.3–0.6	0.8	< 0.2	2.3
Mn	133.4	0.05–0.1	1.3	< 0.1	< 5.0
Mg	361.9	125–150	132.8	1.8	128.3
Ca	543.4	–	649.4	629.7	735.3

[a] [18]

to be calcium sulfate and calcium orthosilicate which increase the cementing action of the agglomerates [12].

4. Conclusions

In this study, the fly ash, a waste product, was evaluated as a binder in conjunction with the Portland cement to mitigate acid mine drainage caused by the reactive tailings. The following conclusions can be made:

(1) The agglomeration behavior of the two acid mine tailings (Noranda and CTC) was studied using two binders (fly ash and Portland cement). The agglomerate properties measured were the crushing strength and the leachability.

(2) Noranda tailings were found to be more chemically reactive owing to the finer particle size and the presence of higher amounts of iron and sulfur bearing minerals than the CTC tailings.

(3) The use of fly ash as a sole binder was found to be inadequate in imparting the required crushing strength, whereas the use of Portland cement alone as a binder provided sufficient strength to the agglomerates prepared from both the tailings. The use of fly ash, however, when used in conjunction with cement increased the crushing strength beyond the values obtained by the use of cement alone. The increase, however, was more pronounced in the case of reactive tailings (Noranda) than less reactive tailings (CTC).

(4) It was found that agglomeration of reactive tailings required 10% cement by weight. In a typical test, the addition of 20% fly ash was found to be equivalent to 5% cement.

(5) The use of fly ash in conjunction with Portland cement also resulted in

immobilization of the heavy metals ions from the Noranda tailings agglomerates, whereas the individual use of these binders did not immobilize the heavy metals.

(6) The use of fly ash with the Portland cement was found to increase the crushing strength and the immobilization of the heavy metals. The concept is therefore economically viable as well.

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