Recovery of Zinc from Waste Material Using Hydrometallurgical Processes

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A lead-zinc ore deposit in Balikesir/Balya, Turkey, was mined and abandoned almost 70 years ego. Nearly 1,000,000 tons of flotation tailings and 300,000 tons of slag, which contain considerable amounts of zinc remain. In this study, an assessment of the technical feasibility of an acidic leach process for the recovery of zinc from slag was considered. The slag contained approximately 29% Fe, 13% Zn, 3% Pb and 2% S. Preliminary leach tests showed that it was not possible to achieve a selective and efficient extraction of Zn from the slag using low concentrations of H_2SO_4 *and low temperatures. This result can be attributed to the proportions of zinc present as oxide and ferrite (*$Zn\ Fe_2O_4$*). This slag composition has a significant effect on treatment options because the oxide is soluble to a varying degree in most leachants, whereas ferrites tend to be insoluble. In order to increase the recovery using extraction, leaching tests were performed in two stages. Slag was first subjected to leaching, and residue was contacted with a hot and more concentrated sulfuric acid solution in order to dissolve the ferrite. The dissolved iron was then recovered from solution by ammonium jarosite precipitation. The optimum conditions to leach the slag were determined: 1.85 N and 4.07 N* H_2SO_4 *at 1/10 solids ratio, at a temperature of 55° C and 95° C in the first and second stages, respectively. Results show that the 77.45% Zn extraction could be achieved by atmospheric leaching. Compared to other processes, such as pressure leaching, ammonia, and NaOH leaching, pressure leaching had the highest extraction efficiency of 87% Zn and 80% Fe, but may have extremely high investment and operation costs.*

INTRODUCTION

Filter dust and slags are typical industrial wastes from metallurgical plants. Slags consist mainly of oxides of the gangue minerals, which can be made fluid at a reasonable temperature by the addition of a suitable flux [1]. Slags have a low solubility for the oxide form of the metals being smelted in order to have a minimum environmental impact when disposed. The lead-zinc plant residues contain unrecovered zinc as zinc ferrite, and lead as insoluble sulfate. Therefore, waste minimization and metal recycling from these wastes have become a major concern in recent years. A process using jarosite seeds is now widely used for the recovery of zinc and other metals. However, the cost of recovering zinc from zinc oxide is lower than the recovery cost from zinc ferrite residue. The main benefit of the jarosite process is that it is an economically viable method to recover metals that might otherwise have little or no value.

The lead-zinc ore deposit in Balikesir/Balya, Turkey, was mined by French companies between 1880 and 1935. The site was abandoned as its silver content decreased. Lead ore was concentrated by gravity separation and flotation processes. Lead and silver concentrates were produced by a pyrometallurgical method. Nearly 1,000,000 tons of flotation tailings and 300,000 tons of slag remain in the area, exposed to oxidation for more than 50 years. During this period, the high sulfur content of the waste products has resulted in the production of acid that has further leached the tailings, resulting in lead contamination of the disposal area.

Several studies were conducted on the reflotation of tailings to reduce waste volumes and toxicity levels, but fewer studies have been concerned with the treatment of slag waste [2]. The purpose of our study was to examine the slag for potential recovery of valuable recyclable metallic constituents, mainly zinc metal. The recovery tests were initially focused on characterization of the slag sample, and then on determining the solubility of metallic compounds by hydrometallurgical methods, i.e., H_2SO_4 leaching. Experimental variables affecting the solubility were leaching time, solution concentration and pressure. The results of sulfuric acid leaching tests were compared to other processes using ammonia and sodium hydroxide.

BACKGROUND

Most zinc concentrates contain significant amounts of iron so hydrometallurgical treatment of zinc sulfide concentrates has been focused on separating zinc from iron. Apart from the direct leaching process, the concentrate need to be oxidized prior to hydrometallurgical treatment. In the roasting process, much of the iron present in the zinc concentrate forms zinc ferrite ($ZnFe_2O_4$), which is insoluble in the dilute H_2SO_4

Table 1. Chemical composition of the different size fractions of Balya slag.

Particle size, µm	Zn %	Fe %	Pb %	S %
106 - 75	13.27	29.38	3.23	2.25
75 - 53	11.33	30.61	3.25	2.27
53 - 45	11.58	30.41	3.25	2.27
45 - 38	11.72	31.22	3.25	2.27
-38	11.78	31.22	3.25	2.27

commonly used in the leaching process. Research on this problem showed that most of the zinc and iron in the ferrite dissolves readily in concentrated sulfuric acid solution at the temperature around the boiling point of the solution. The problem was how to precipitate iron from solution. The separation process was costly and required special pressure filters.

In the early 1970s, the ferrite problem was solved by researchers from Norzink, EZ, and Asturiana companies who discovered that iron in zinc sulfate solution obtained by hot acid leaching could be separated in a crystalline, easy to filter, jarosite form. The beneficial use of jarosite—(M $(Fe_3(SO_4)_2(OH)_6$ in which M is Na, or NH_4)—particles as seeds in the precipitation step has been successfully used in several plants, as well as in treating residues. This process has also been used to treat residue from large stockpiles [3, 4].

On the other hand, metallic zinc and zinc oxide are selectively dissolved in aqueous ammonia solution to form amine complexes according to Equations 1 and 2:

$$ZnO + 4\,NH_3 + H_2O \rightarrow Zn(NH_3)_4^{+2} + 2OH^- \quad (1)$$

$$Zn + 1/2\,O_2 + NH_3 + H_2O \rightarrow Zn(NH_3)_4^{+2} + 2OH^- \quad (2)$$

Iron oxides, hematite, and magnetite, which are the principle impurities in slag, mainly occur with zinc or zinc oxide, and are insoluble in an ammonia solution. Actually, ammonia ions alone do not dissolve the zinc, but when added to an ammonium carbonate and ammonium hydroxide solution, they increase the rate of dissolution as a result of inhibiting the ionization of ammonia [5, 6]. Zinc oxide is also soluble in an NaOH solution. The solution, when electrolyzed, yields zinc in powder form.

A recent addition to the electrolytic process is the utilization of pressure leaching of zinc sulfide concentrates, developed by Sheeritt-Gordon. Pressure leaching, in which the zinc sulfide concentrates are leached directly to produce zinc sulfate, offers distinct advantages over the conventional roast-leach route. The process is conducted at 150° C and 700 Kpa oxygen pressure. The following reaction occurs:

$$ZnS + 2H^+ + 1/2\,O_2 \rightarrow Zn^{+2} + S + H_2O \quad (3)$$

The advantages of the process are simplicity, effectiveness, environmental-friendliness, and flexibility in feed materials. Therefore, it has found commercial applications [7].

EXPERIMENTAL

Materials

A slag sample was taken from the waste area of the Balya mine. A 2 kg sample was crushed in a jaw crasher, and the -2 mm size fraction was place in a laboratory ceramic mill for further size degradation. Each 100 g of sample was ground for 2 hr and classified by wet screening. Chemical analyses of classified fractions were performed by standard spectrophotometric methods (AAS). The results of chemical analyses are given in Table 1.

The data in Table 1 shows that the Zn content of the classified sample slightly decreases for particles finer then 75 µm, but Fe content increases. The XRD analyses were carried out using a S5000 diffractometer, with a nickel filtered Cu Kα radiation. Scattering intensities were obtained from 20° to 60° (2θ), by scanning at 0.5° (2θ) steps. The identified phases, using the JCPDS mineral and inorganic powder diffraction files, indicated that slag mainly consists of sphalarite/wurtzite, zincite magnetite, and lead oxide. The higher content of zinc sulfide can be explained by the distribution of very tiny sphalarite particles in an amorphous or partly crystalline silicate matrix that were unreacted during previous stages and concentrated in slag (See Figure 1).

Leach Experiments

Zinc can be most conveniently recovered utilizing the Jarosite process. However, other alternative leaching methods, such as those using ammonia-ammonium carbonate, sodium hydroxide, and pressure acid leaching, have also been employed to obtain greater selectivity. The experimental flow sheet, showing all extraction processes, is found in Figure 2.

Atmospheric H_2SO_4 acid leaching experiments were carried out in a 250 ml glass flask placed on a heated magnetic stirrer. All experiments were performed using a 10% solid mixture and 16 ml of sulfuric acid (5.92 N). These conditions were determined to be optimum in a previous study [8]. A 10 g sample of slag powder was added in to the preheated 100 ml acidic solution, and continuously stirred for 2 hr. To evaluate the effect of reaction time on zinc dissolution, the pH of the solution was measured every 10 min. In the first stage of extraction tests 100 ml of 0.37, 0.55, 0.92, and 1.85 N H_2SO_4 solutions were used, respectively. The solution concentrations were adjusted by the addition of 1, 1.5, 2.5, and 5 ml of H_2SO_4 (98%) to the distilled water. During the first extraction period, the temperature was maintained between 50 and 55° C. The liquid was then carefully

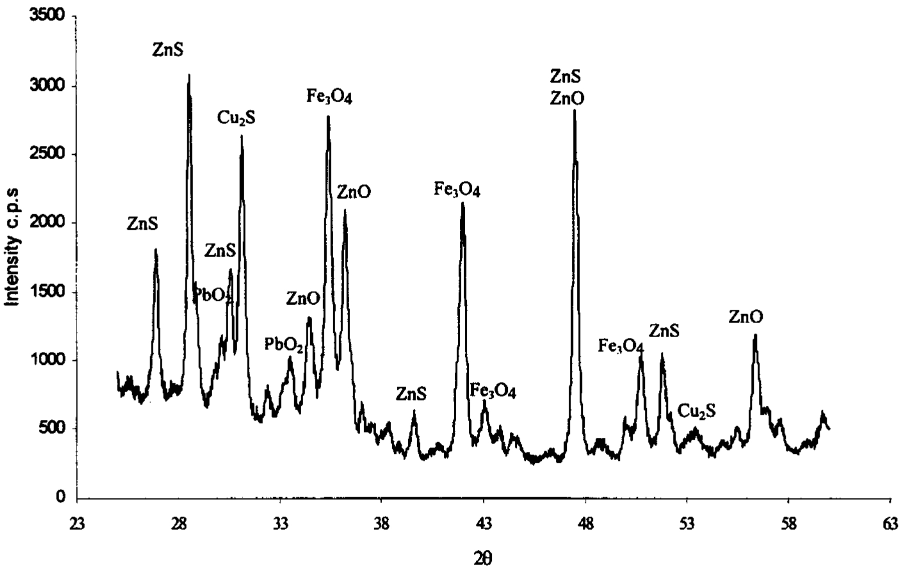

Figure 1. XRD diffractogram of Balya slag.

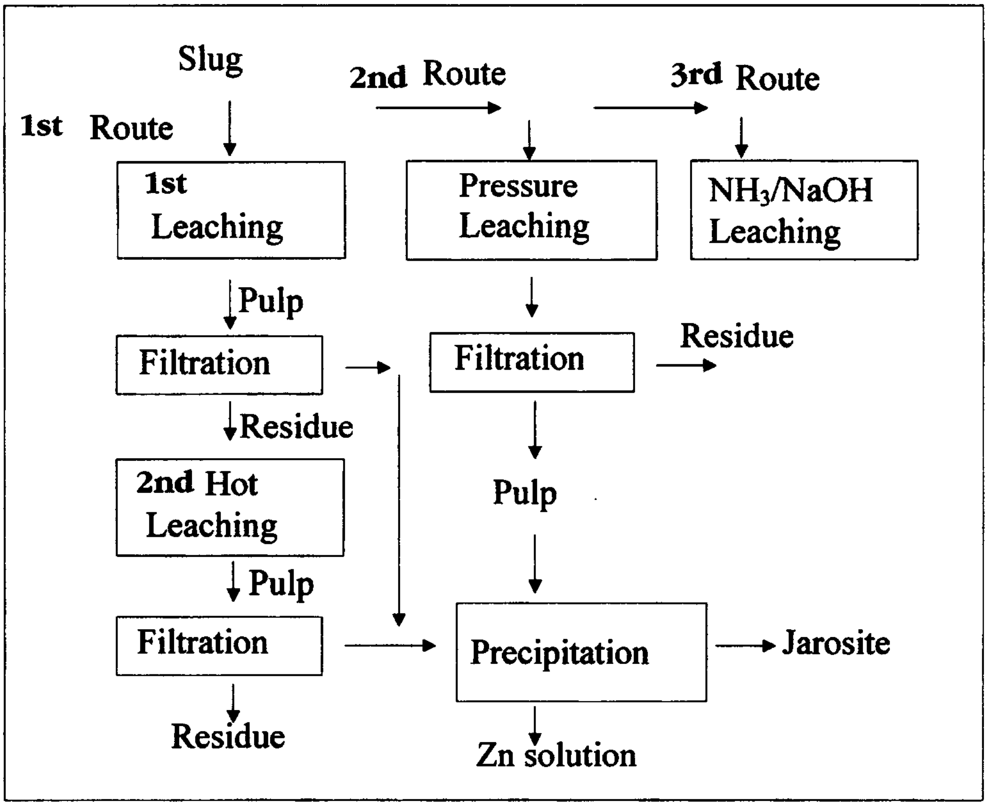

Figure 2. Experimental flow sheet of alternative extraction methods for Balya slag.

filtered using a buchner funnel and kept for analysis. The residue from first stage was then releached using a more concentrated sulfuric acid solution which was prepared by adding the rest of the predetermined amount of acid at a temperature of 95° C. After filtration to remove solids, the pH of the filtrate was increased to 1.5 with NaOH. The dissolved iron in the solution was precipitated as jarosite by adding the ammonia-ammonium carbonate solution at 95° C.

A series of experiments was also performed to determine the effect of particle size on zinc dissolution. Different size fractions (-106 + 75, -75 + 53, and -38 μm) were tested as a feed material.

The pressure leach experiments were performed in an autoclave. Experiments were run with an 10 g of

Table 2. Results of sequential extraction test of slag.

H_2SO_4 Concentration (first and second stages)	0.37 N + 5.55 N	0.55 N + 5.36 N	0.96 N + 4.95 N	1.1 N + 4.81 N	1.85 N + 4.07 N
1st stage Zn Conc. mg/l	113	360	476	508	626
2nd stage Zn Conc. mg/l	534	382	330	323	226
Total Zn Conc. mg/l	647	742	806	831	852
1st stage Fe Conc. mg/l	138	291	610	740	1817
2nd stage Fe Conc. mg/l	1700	1669	1600	1580	725
Total Fe Conc. Mg/l	1838	1960	2210	2320	2542
Extraction % Zn	58.81	67.45	73.27	75.54	77.45
Extraction % Fe	55.69	57.87	64.54	70.30	77.03

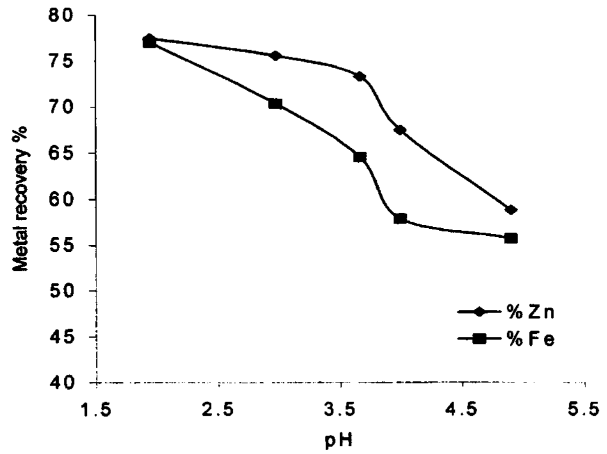

Figure 3. Final extraction percentage of metals measured against pH in the first leaching step.

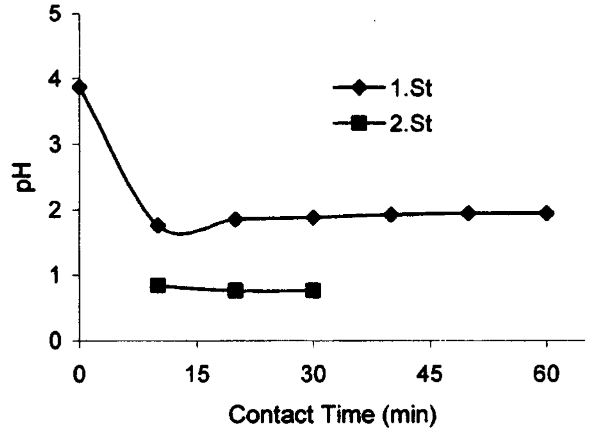

Figure 4. Relationships between pH and contact time for the first and second stages of metals extraction from slag.

106 - 75, 53 - 45, and -38 µm size fractions under 700 kps pressure for 2 hr in order to evaluate the influence of pressure and particle size effect on zinc extraction. The effect of solution concentration on zinc extraction recovery was also tested for -38 µm size fraction with increasing concentration: 1.1, 1.85, 3.7, and 5.92 N of H_2SO_4. The zinc and iron concentrations were determined in final solutions after leaching tests were completed by AAS. The composition of selected leached residue was also determined by X-ray diffraction analysis.

RESULTS AND DISCUSSION

Sulfuric Acid Concentration Effect

The dissolution amounts of both iron and zinc in solution for different acid concentrations, and the calculated recovery amounts via acid leaching are given in Table 2. For the Fe^{+3}-SO_4-H_2O system at 25° C, the simplest hydrated Fe^{+3} ion is stable at low iron concentrations, but, as the hydroxyl ion is added to the system, a series of Fe^{+3}- hydroxyl complexes is formed. At ferric ion concentrations greater than the 10^{-3} M, a dimerized species ($Fe_2(OH)_2^{+4}$) predominates, and the extent of hydrolysis increases with increasing temperature [9]. Therefore, the first stage of the extraction test was started using 0.37 N H_2SO_4 as an extracting reagent (the final solution pH of first stage leaching was approximately 4.90) to obtain clear/pure Zn solutions, or to precipitate iron ions and separate them by filtration. Hence, the concentration of the acid solution was gradually increased to 1.85 N to observe the effect of H_2SO_4 concentration on the extraction process. As expected, dissolution of Fe ions in solution decreased with decreasing acid addition at the first stage of leaching, but the total zinc extraction recovery also decreased.

In Figure 3, the measured final solution pH in the first leaching step is plotted against the percent of both iron and zinc obtained in final extraction recoveries using predetermined acid concentrations. The results clearly indicate that the total recovery of metals depends on pH. The total extraction percentages of zinc increased from 58.81 to 77.45% by using greater amounts of acid (0.37 to 1.85 N) in the first leaching stage. For that reason, further experiments were performed with 1.85 N and 4.07 N H_2SO_4 solutions in the first and second stages, respectively. To remove dissolved Fe ions from solutions, the first stage filtrate solution was mixed with the second stage solution before jarosite precipitation. Under the conditions described above, the

Table 3. Effect of leachants on zinc recovery.

Leachants	Time h	Zn mg/l	Recovery %
Sulfuric acid	2	852.00	77.45
Ammonia	2	118.80	10.80
Sodium hydroxide	2	142.88	13.00

Table 4. Relationship between leached amount of metal and particle size.

Size fraction µm	Zn mg/l	Fe mg/l	Zn recovery %	Fe recovery %
-106 +75	720	2,300	65.45	73.33
-75 +53	747	2,415	67.90	75.13
-38	852	2,542	77.45	77.63

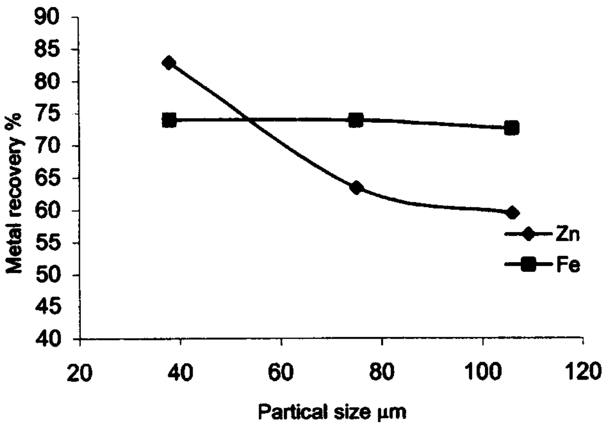

Figure 5. Dissolution of zinc and iron from variable particle size fractions of slag in 3.7 N H_2SO_4 at 10% solids, under 700 kps pressure for 2 hr.

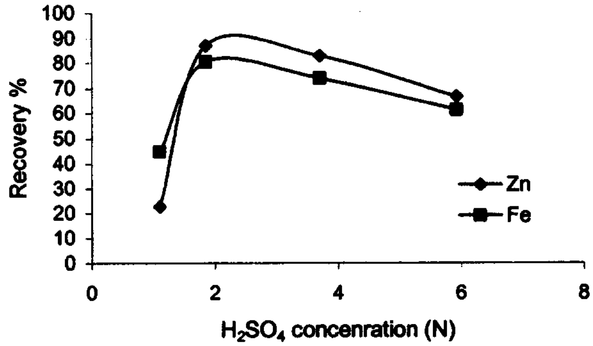

Figure 6. Zinc and iron extraction curves of -38 µm size fraction sample for increasing acid concentration.

jarosite precipitation provided 95% removal of the iron from feed solution. The iron, lead, and copper contents of the solution were negligible.

Contact Time

It was observed that, during first stage of leaching, the pH of the leach solution increased slightly with increasing contact time up to 40 min. At that point, the dissolution of zinc reached equilibrium. In contrast, the reaction was completed in 20 min in the second stage (See Figure 4).

Leaching Agent

Several leaching agents can be used to extract zinc from ore concentrates and slag. The most common leachants, other than sulfuric acid, are ammonia-ammonium carbonate (AAC), and sodium hydroxide. The AAC tests were performed using 50 mL of ammonia and 20 g of NH_4CO_3 in 100 mL solution at 10 % solids and 55° C for a 1 hr contact time. The pH of leach solution decreased from 11.20 to 9.59 in first 30 min After this period, no further change in pH was detected.

Tests with NaOH were carried out utilizing the following conditions: 4M NaOH, 10% solids, 70° C, and 1 hr contact time. The calculated extraction percentages of zinc are given in Table 3. The results clearly indicate that H_2SO_4 is the best leaching reagent for the recovery of zinc from Balya slag. These results can be attributed to the proportions of zinc present as an oxide or sulphide and ferrite. Zinc ferrites tend to be insoluble in conventional alkaline processes.

Influence of Particle Size

The effect of particle size on the dissolution of zinc and iron was tested using a 5.95 N H_2SO_4 solution on 10% solid mixture for a 2 hr total contact time (first and second steps). The experimental results demonstrated that the extraction of zinc and iron increased with the decreasing particle size (Table 4.). When the particle size decreased from 106 to 38 µm, the recovery of zinc increased from 65.45% to 77.45%. This result can be explained by the higher contact area for smaller particle sizes.

Pressure Leaching

The influence of particle size on the zinc and iron extraction for 3.7 N H_2SO_4 solutions at 10% solids and 700 kps pressure for 2 hr contact time is given in Figure 5. Decreasing the particle size from 106 to 38 µm increased the zinc extraction percentage from 60% to 83%. But no significant difference in the amount of dissolved iron was observed.

Pressure leaching of a 38 μm size fraction of sample at 700 kps pressure with 1.1 N H_2SO_4 provided only 22.72% Zn and 44.84% Fe extraction percentages, while leaching in 1.87 N H_2SO_4 increased the extraction efficiency to 87% Zn and 80% Fe, respectively. A further increase in acid concentration resulted in decreasing both zinc and iron content of the extraction fluid. This decrease can be explained by the classic phase equilibrium studies of Posnjac and Mervin [10]. According to their work, at higher temperatures (close to 200° C), and higher H_2SO_4 concentrations, which can be present initially or generated by reactions, the solubilities of iron and zinc are decreased quite markedly due to precipitation of zinc-iron complexes. The optimum extraction conditions were found: -38 μm particle size, 1.87 N H_2SO_4, 10% solids and a 2 hr contact time.

CONCLUSION

The treatment of Balya mine waste has received increasing attention in recent years. The high sulfur content of flotation waste has resulted in the production of acid and further leaching of tailings. However, the slag is still in solid form, and is not classified as a hazardous waste. It would still need to be disposed of in a specific site or controlled landfill. Disposal of the waste at a controlled landfill is costly. For that reason, recovery or recycling of this waste as a possible alternative to disposal is attractive. In this study, we found that 77.45% and 87% of zinc can be extracted by both atmospheric sequential acid leaching and pressure leaching. Leaching in an autoclave has a higher recovery fraction then atmospheric leaching. However, pressure leaching requires an extremely high investment cost and high operation costs. It can be concluded that the sequential atmospheric acid leaching process described in this paper appears to be a technically feasible method of recovering zinc from Balya mine slag.

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