THE RECOVERY OF MANGANESE AND GENERATION OF A VALUABLE RESIDUE FROM FERROMANGANESE SLAGS BY A HYDROMETALLURGICAL ROUTE

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ABSTRACT

Ferromanganese slags contain appreciable percentages of manganese, mainly in the form of silicate phases. The manganese values may be leached from the slag using sulfuric acid. This approach has two problems. One is the consumption of sulfuric acid, which might add a considerable cost to the recovery process. The other problem is the reliable handling of the silicate content to prevent the formation of gelled phases, which would make solid-liquid separation after leaching impossible.

A possible solution to both problems would be the optimization of the leaching residue so that it adds value to the process. This could be done if the leach residue, which contains the silicate materials, can be formed in a way that would leave the silica content as amorphous or micro crystalline phases. Such a residue could be a valuable additive to Portland cement.

Investigations of the leaching process have shown that the manganese may be recovered in excess of 90%, at industrially useful concentrations. A variety of recovery processes for manganese from such solutions are possible; for instance precipitation as oxide or carbonate or crystallization as sulfate salt. It has been shown that the formation of silica gels may be avoided using suitable leaching procedures.

The leaching residues have been found to contain substantial amounts of amorphous silica and calcium sulfate. Several of these residues have been tested as additive to Portland cement. Important parameters such as the hydration characteristics, flexural- and compressive strength have been measured. It was found that such addition is beneficial for the development of additional compressive and flexural strength as compared to normal Portland cement.

KEYWORDS: *manganese, ferromanganese, slag, leach residue, Portland cement, additive.*

1. INTRODUCTION

Ferromanganese (and silicomanganese) production lead to the formation of slags, which contain considerable amounts of unreduced manganese, and are typically discarded on slag heaps. Approximately 20 million tons have accumulated on slag dumps in South Africa and a further 0.5 million tons are added every year. These slags constitute an environmental risk but are also potential sources of valuable manganese if a suitable method of recovery could be found. Ideally, the slag would be returned to the furnaces, but build-up of problem elements such as alkali metals and zinc limit the amount of recycling possible.

A hydrometallurgical route could be used to prevent the problem of impurity build-up.
The manganese slags contain high silica, but very little iron and as a result, the usual iron removal procedures associated with leaching manganese from ores are unnecessary.

However, the presence of amorphous silica can result in solid-liquid separation problems due to the formation of gels. If the silica gelling problem can be managed, it might be possible to recover the amorphous silica, which is a valuable component of Portland cement. The hydrometallurgical route could therefore produce more than one product with commercial value: a manganese-bearing product such as an oxide, carbonate or manganese sulfate salt to be sold into the manganese industry or re-introduced to the smelter, as well as an amorphous silica-bearing product to be sold into the cement industry.

Prior work by various authors on the reduction or leaching of ferromanganese slags has been reported in an earlier paper [1]. The leaching processes that were investigated included leaching by dilute sulfuric acid, hydrochloric acid and ferric chloride solutions.

Silica fines, as silica flour, micro silica and nano silica are sometimes added to commercial cements and concretes. Generally, these silica products are produced by high temperature vaporization of silica, low temperature ageing of sol-gel silica or the precipitation of nano-silica. Strong interest from the building industry comes from the positive effects obtained by the addition of micro- and nano-silica to concretes: reduced porosity, reduced permeability, reduced chemical attack, reduced efflorescence; increased sulfate resistance, increased compressive strength, increased thermal stability, and accelerated hydration. Prior work on the use of-, and reactions of silica in cement has been reported in an earlier paper [1].

All reported additions of silica to concrete are based mainly on rather pure materials. In this study a leach residue is used containing also calcium sulfate (hydrates). Therefore the amount of addition is determined by the optimal amount of sulfate added to the cement clinker for hydration control; with the nano-silicate also present enhancing the properties of the cement. Without treatment, the slag can also be used as a pozzolanic additive [2] giving some increased hydration reactions when used in moderate amounts up to 20%. By addition of untreated slags it is possible to gain some reduction in CO_2, but then the manganese values are lost.

Work done on the leaching of ferromanganese slags is scattered and incomplete in the literature. This study is therefore unique and comprehensive by the fact that it considers the extraction of manganese values from ferromanganese slags using hydrometallurgical methods, and uses the leach residue as a cement additive. It is therefore envisaged that the environmentally undesirable slags be re-used in total so that they can be permanently removed from the environment.

2. FERROMANGANESE LEACHING PROBLEM

Ferromanganese slags contain silicate phases and their leaching produces soluble silicates. This forms silicic acid which can polymerize to silica gel $(SiO_2)_n$ and thus render solid-liquid separation difficult [3]. To minimise silica polymerisation during digestion, this work uses the quick leach or water starved model [4]. This paper presents experimental work done at the University of Pretoria in South Africa and at the Martin Luther University in Germany on sulfuric acid digestion of ferromanganese slags, followed by water-leaching of the acid leach residue, and the use of the final water leached residue as a Portland cement additive. The University of Pretoria through its Department of Materials Science and Metallurgical Engineering is focused on the hydrometallurgical route, and the Martin Luther University through its Department of Mineralogy/Geochemistry on the use of the leach residue as cement additive.

3. MATERIALS AND METHODS

Most of the experimental detail is described in an earlier publication [1].

Digestion was done by adding a stoichiometric quantity of acid to a 1:1 solid:liquid slurry of 100 g slag, except as noted in the text. After cake maturation of 24 h the residue was leached using a single batch of 400 ml distilled water. For the determination of leaching rate from the digestion residue, 300 ml water was used to re-pulp the residue. The slurry was stirred by magnetic stirrer. The effect of sequential washing stages was determined similarly, but using a fresh 300 ml portion of water for each stage of 30 minutes.

4. RESULTS AND DISCUSSION

4.1. Ferromanganese slag chemical- and phase analysis

Table 1 gives typical composition ranges obtained by XRF for the ferromanganese slag. Iron is low. In table 2 the mineral composition is tabulated. The major phases are silicates, with manganese as Mn (II) present in two phases: Glaucochroite and Manganosite. The amorphous content of the ferromanganese slags is high, approximately 30 %.

Table 1: Chemical analysis of ferromanganese slag

Oxide	Mass percent
MnO	28.0 – 30.0
SiO_2	28.0 – 30.0
CaO	28.0 – 30.0
MgO	6.0 – 6.5
Al_2O_3	5.0 – 5.5
Fe_2O_3	1.0 -1.3

Table 2: Phase analysis of the ferromanganese slag

Mineral	Chemical structure	Mass percent
Glaucochroite	$CaMnSiO_4$	55.00 – 65.10
Manganosite	MnO	2.28 – 4.50
Gehlenite	$Ca_2Al[AlSiO_7]$	4.00 - 8.49
Monticellite	$CaMgSiO_4$	0.00 – 2.00
Quartz	SiO_2	0.00 – 5.10
Amorphous	-	21.00 – 30.0

4.2. Particle size analysis

Figure 1 gives the cumulative mass percent particle size distribution of the milled ferromanganese slag used in this work. Analysis of the size fractions showed that the manganese is fairly evenly distributed between these size fractions; this is also shown in figure 1.

4.3. Effect of acid concentration

The effect of acid concentration on the leaching process was determined by adding a stoichiometric amount of acid to the dry slag. Figure 2 shows the effect of acid concentration on residual manganese in the leach residue. At low acid concentrations the residual manganese in the leach residue is high, but low at high acid concentration. This trend can be explained by the fact that at acid concentrations below ca. 20%, sulfuric acid is not able to completely destroy the silicate matrices of the minerals contained in the ferromanganese slag. In this work, concentrated sulfuric acid is used because lower concentrations are susceptible to silica polymerisation at the digestion or cake preparation stage or after solid liquid separation.

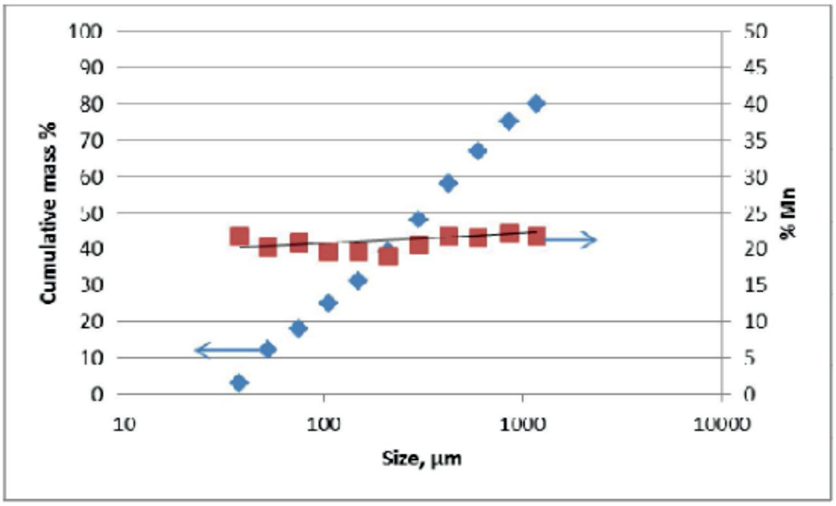

Figure 1: Ferromanganese slag particle size distribution and manganese content

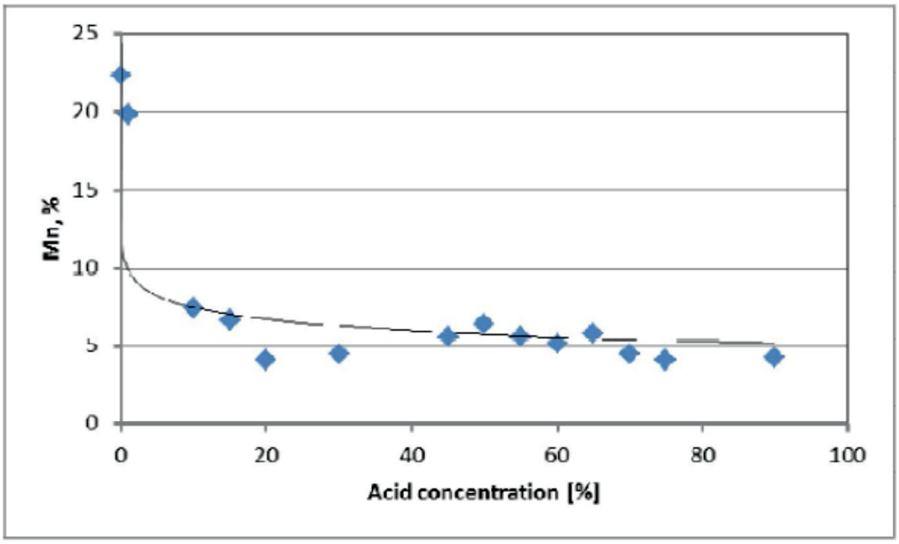

Figure 2: Residual manganese in the leach residue vs. acid concentration

4.4. Effect of particle size on leaching

It was found that the slag particle size has little effect on the extent of leaching under the experimental conditions employed, until the size exceeds 600 µm.

This is illustrated in figure 3 which shows the residual manganese content in the solid residue after water leaching. Larger particles would be expected to require long leaching times. This is exacerbated by some of the leaching reaction products being insoluble (e.g. calcium sulfate) which would slow the leaching reaction, especially of larger particles. Solution concentrations as high as 65 g/l were obtained.

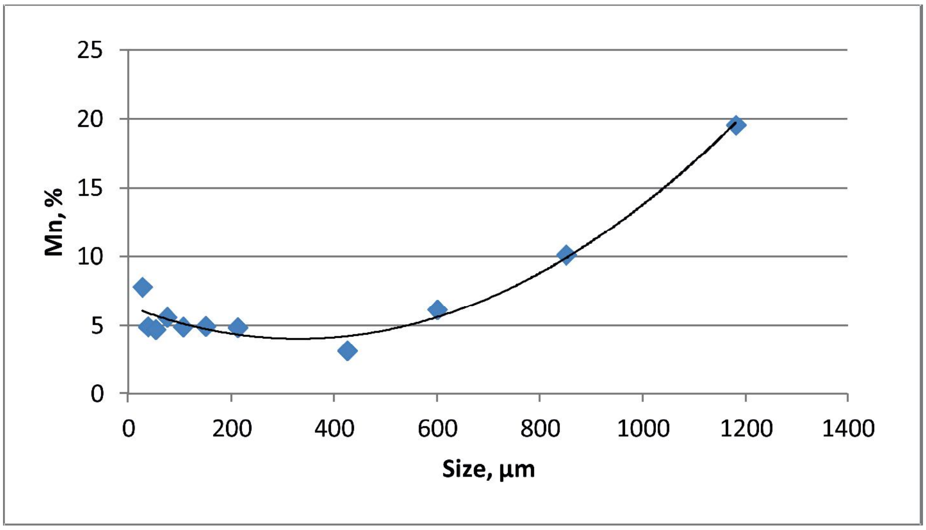

Figure 3: Manganese in the leach residue vs. particle size

4.5. Leach residue analysis

The leach residue consists mainly of amorphous silica and calcium sulfate compounds. Depending on the degree of hydration, one can obtain anhydrite, calcium hemihydrate or calcium dihydrate (gypsum). Table 3 gives typical chemical compositions of two extreme leach residues (samples 1 and 2) with residual manganese contents of 4.54 and 4.47 % respectively. Table 4 shows a leach residue phase composition after 15 minutes of contact time with water, whereas table 5 shows a residue phase composition after 60 minutes of contact time with water.

Table 3: Chemical composition of leach residue

Oxide	**Weight Percentage**	
	Sample 1	**Sample 2**
SiO_2	20.76	20.90
Al_2O_3	1.00	0.90
Fe_2O_3	0.26	0.37
MnO	5.86	5.77
MgO	1.35	1.31
CaO	19.81	21.64
SO_3	18.88	21.71
LOI	31.28	26.53

Table 4: Phase composition of a leach residue with 4.54% residual manganese. (Graphite is a residue of the reductant used in ferromanganese production)

Mineral	**Chemical formula**	**Percentage**
Amorphous		46.87
Anhydrite	$CaSO_4$	2.71
Graphite	C	2.19
Gypsum	$CaSO_4 \cdot 2H_2O$	48.23

Table 5: Phase composition of a leach residue with 4.47% residual manganese

Mineral	Chemical formula	Percentage
Amorphous		41.45
Graphite	C	1.07
Gypsum	$CaSO_4 \cdot 2H_2O$	57.48

4.6. Water leaching kinetics

After the initial digestion step, the manganese values are leached from the digestion solids. The rate of manganese leaching was determined using a single step batch leach. As shown in figure 4, about 66 % of the manganese is leached in less than 60 minutes. Increasing the lixiviant temperature, and rate of stirring, as well as solid to liquid ratio may be expected to improve the leaching rate. This has not yet been tested. A multi-stage, counter-current leaching approach is also likely to improve the rate of manganese removal from the digestion solids. Figure 5 shows that very little manganese is extracted at and after the third stage. The water leaching step should thus comprise of two or three counter-current stages.

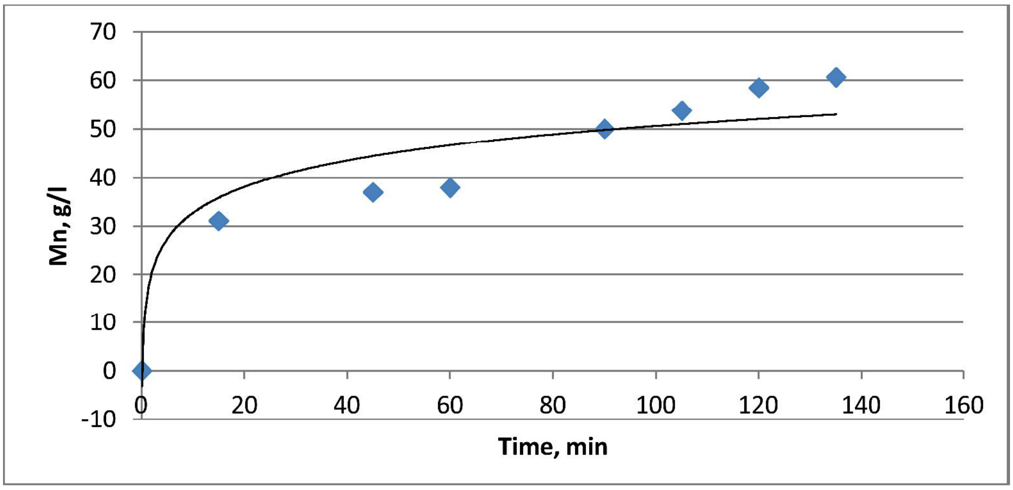

Figure 4: Manganese in the leach solution vs. time

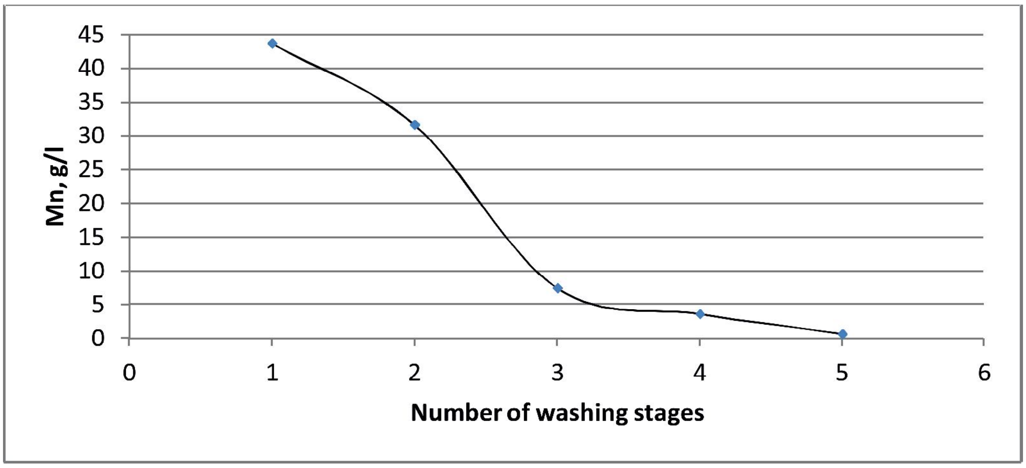

Figure 5: Manganese in the wash solution vs. washing stage

4.7. Pregnant leach solution analysis

The manganese content in the pregnant leach solution was as high as 40 to 60 g/l. This relates to a recovery of between 75 % and 95 %, depending on the number of water leaching stages. It has been observed that when the cake is water leached in 3 stages, the manganese recovery is as high as 95%. Table 6 presents typical analyses of the pregnant leach solution for elements other than manganese. For this solution to be suitable for manganese electrowinning, the manganese concentration would have to be 30 g/l minimum, and the iron and silicon contents have to be lower than 15 and 10 g/l [5, 6] respectively.

Table 6: Typical concentrations of different elements in the pregnant leach solution

Na	**Mg**	**Al**	**K**	**Ca**	**Fe**	**Si**
mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
15 - 20	4 - 6	1 -2	1 -5	75 -80	240-250	40 -70

4.8. Cement addition

The addition of the leach residues to cement was performed with the purpose of determining the effect of the sulfate content which acts as retarding agent for the aluminate phase. Some attempts were also made with supersulfated mixtures up to 10% to see the effect on hydration. The results on strength development appear very promising. The following diagrams show flexural and compressive strength development of an ordinary Portland cement (OPC) clinker without and with addition of leach residue. Figure 6 shows the compressive strength development of OPC (series 1) and OPC plus leach residues obtained by leaching with various H_2SO_4 concentrations (series 2, 3 and 4). The following mixtures were used:

- Series 1: OPC, no addition.
- Series 2: OPC + leach residue (leach residue of 15% H_2SO_4).
- Series 3: OPC + leach residue (leach residue of 50% H_2SO_4).
- Series 4: OPC + leach residue (leach residue of 98% H_2SO_4).

All trials were performed with a water to solid (w/s) ratio of 0.7 to avoid influence of different water to solid ratios. Despite the differing water demands of the different mixtures, the addition in future of a water reducer can positively influence the workability and the final properties.

The influence on the flexural strength development of an OPC with the addition of 3 different leach residues is shown in figure 7.

It is clearly evident that the addition of leach residues improves the strength development. The additions of the three different leach residues produced promising results, with the increases in strength being fairly similar. However, it may be seen that the 15 % leach residue shows the lowest increase in strength of the 3 additions, due to the fact that the slag had not yet reacted completely. In this case some pozzolanic reaction from the undissolved slag also participates in the hydration.

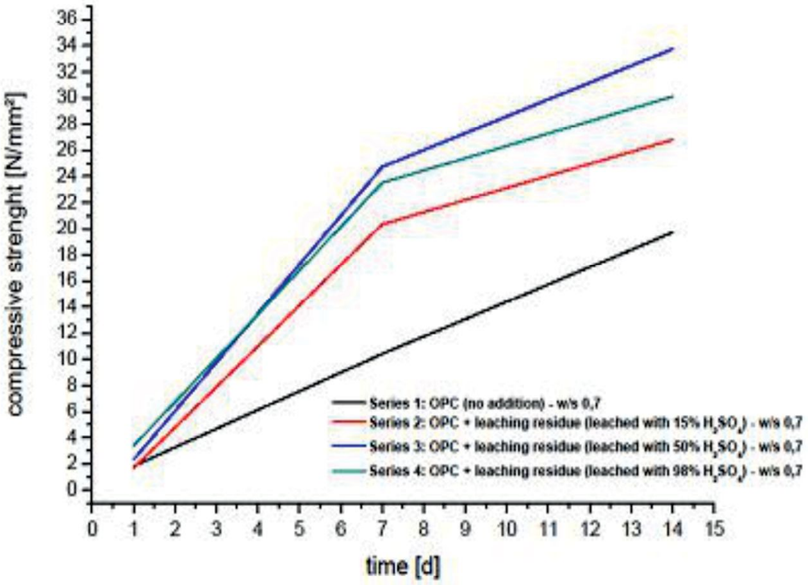

Figure 6: Evolution of compressive strength of OPC and OPC + 3 different leach residues

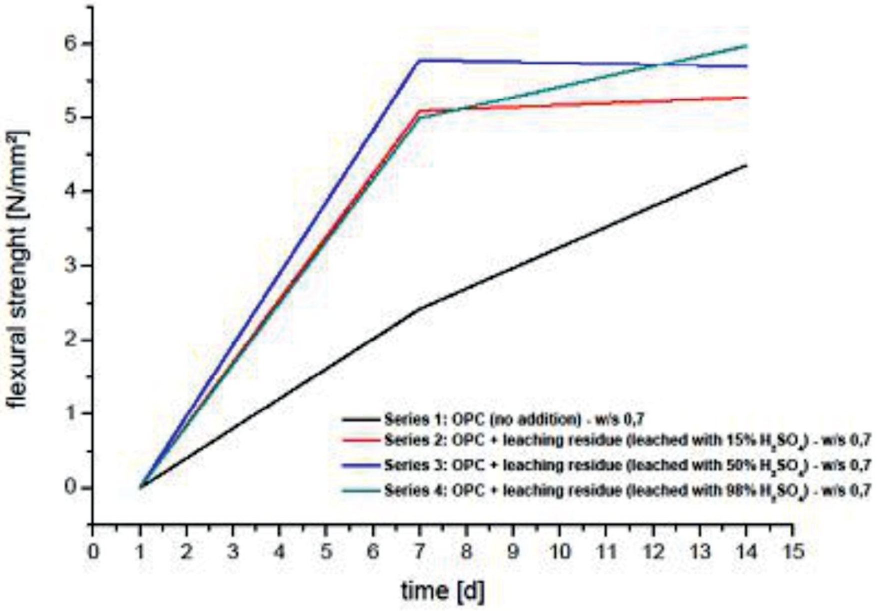

Figure 7: Evolution of flexural strength using a w/s-ratio 0.7 with additions of different leach residues

5. SUMMARY AND CONCLUSIONS

It has been shown that ferromanganese slag can be efficiently digested in sulfuric acid and the resulting cake then water-leached. The water leaching produces manganese sulfate solutions with high manganese contents, and low impurity contents. It appears that the leach solutions would be a suitable feed for a variety of recovery methods. These could include the production of electrolytic manganese metal, battery grade electrolytic manganese dioxide, manganese sulfate crystals for animal feeds and fertilizers, or various chemical compounds such as oxides or carbonates. It has been shown that the SiO_2 in the leach residues participates in the setting reactions of cement and can enhance the hydration, as well as the strength development of the cement mixtures. The work is ongoing and currently aspects such as the optimisation of the digestion and leaching steps, methods of manganese recovery and optimization of leach residues for cement addition are under investigation

6. ACKNOWLEDGEMENT

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