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STUDY ON CHEMICAL AND MINERALOGICAL COMPOSITION OF BLAST FURNACE SLUDGE FOR INTRODUCTION TO THE SINTERING PROCESS

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Abstract: The blast furnace sludge is a waste product of the steel industry which is produced in considerable quantities and there is permanently concern to use them, to limited environmental pollution. Our work presents the chemical and mineralogical characterization of the blast furnace slurries for the preparation of ultrafine ferrous slurries resulting from the process of obtaining cast iron in the blast furnace. The main chemical elements, from XRF analysis are as iron, calcium, silicon, magnesium, combined in chemical compounds such as silicates, silicon oxide, hematite or magnetite. The sintering laboratory tests using sludge showed better results for the proportion of minerals that include iron and its oxides in the ferrous agglomerate, compared to the furnace sludge, from XRD measurements and SEM-EDX analysis. It is a possible to use them on the existing industrial flows, introduction into the agglomeration batch, in order to obtain the ferrous agglomerate needed for the technological process in the furnaces. In this way, there is a solution, to reduce significantly environmental pollution by avoiding their handling, transport, and storage in open dumps and preventing contact with human settlements.
Key words: blast furnace sludge, agglomeration, chemical, mineralogical analysis.

1. INTRODUCTION

In industrial processes, metallurgical and especially steelmaking, in addition to the main product (cast iron, steel and ferroalloys), ferrous waste results, which can be recycled in steelmaking and their recovery is a permanent concern in order to protect the environment [1-4]. In the steel industry, powdery waste results: dust and sludge from coke ovens, dust and sludge from agglomeration and furnaces, dust and sludge from steel mills, tunder sludge from lamination, sludge from metal coatings, etc.

The choice of the recovery process and technology must take into account both the characteristics of the waste, the destination of the product obtained and the existing processing facilities in the waste area. Of particular interest is the non-conventional waste recycling processes in order to obtain a product with a high content of metallic iron [5]. In the process of making pig iron in the furnace, waste called furnace sludge is produced, which is stored in landfills, being considered a polluting factor of the environment. Due to the content of aluminosilicates, mainly amorphous substance and clays, and following atmospheric weathering, it can agglomerate naturally forming consistent and mechanically resistant lumps.

Blast furnace slurries constituted and continue to constitute manufacturing waste, in their composition there are useful elements such as iron and iron compounds, coke dust, various metal oxides, but also undesirable elements such as earth and clays. Over time, they were stored in landfills and under the action of environmental factors they became polluting products for the environment. Sludges from the point of view of chemical and granulometric composition can be exploited by recycling, and the choice of technology must take into account all their qualitative characteristics [1, 2, 5]. The furnace sludge is separated following the processes of fine purification of the furnace gas resulting from the elaboration of pig iron, but its physical state makes it difficult to handle it directly in the technological flow. The high humidity (30 – 40 %), the micron granulation and the existence of volatile components from the coal injected into the vents make this by-product to be carefully analyzed before being introduced into the composition of the agglomeration batches [1]. The agglomeration of iron ores allows the limited consumption of very fine-grained slurries, but the reverse process also limits the consumption of classic ore dust. Also, their handling and agglomeration batches generate large amounts of dust that disperse into the atmosphere, constituting an important source of pollution with fugitive emissions (PM 10) that can be identified at distances of about 10-15 km.

By introducing these furnace slurries in a dusty state into the agglomeration flow, in significant quantities, a

decrease in the density of the homogenized mass of the charge can be produced, which can have the direct effect of decreasing the productivity of the ferrous agglomerate, of decreasing the mechanical strength of the ferrous agglomerate [2, 6, 7].
However, by optimizing the agglomeration/sintering technology, which currently differs from the classical one, the temperature of the melting layer can be increased up to 1350-1400°C, at which temperature zinc, cadmium and a good part of the lead existing in slurries such as and the dusts resulting from the existing steel technological flow [8, 9].
The advantage of agglomeration technology is that it provides a solution for all ferrous pulverulent wastes generated regardless of the content of iron or non-ferrous elements [5, 7]. Although measures to recycle blast furnace sludge via the pretreatment route have been reported in the literature, there are still challenges [10, 11].
In this paper, we present the chemical and mineralogical analysis of blast furnace sludge, a product used for experiments in obtaining ferrous agglomerate, with the aim of reuse as a by-product in order to limit environmental pollution. Samples of blast furnace sludge and agglomerate were characterized using different methods (XRF, XRD and SEM-EDX). The main advantage of agglomeration technology, starting with laboratory experiments, is that it offers solutions for the recycling of huge quantities from landfills and that are generated continuously.

2. MATERIALS AND METHODS

Furnace sludge samples were taken from the storage dumps of a steel plant, in the amount of 500 g, samples that were well homogenized, and 5 aliquot samples of 100 g each were made after drying.
An identical amount of the same blast furnace sludge samples was used in the agglomeration process, in an IR combustion furnace - type VULCAN - Fusion Technology, using the melting method according to the fusion technique established by Fernand Claisse [8]. The sample processing process in the combustion furnace is similar to the sintering process in the agglomeration machine [12, 13].
The blast furnace sludge taken to determine the chemical, morphological and structural composition was analyzed and processed by melting, following the fusion technique established by Fernand Claisse, in a specialized chemical laboratory, using a lithium tetraborate binder.
Knowing the chemical composition is important in the agglomeration process for the subsequent valorization of the resulting material [13]. The semi-quantitative analysis of the compounds in the samples was carried out using a binder - lithium tetraborate - in an amount 10 times greater than the amount of sample used (10 g of lithium tetraborate per 1 g of sludge sample). The histogram in Figure 1 presents the semi-quantitative percentage analysis of the important compounds from the blast furnace sludge sample.

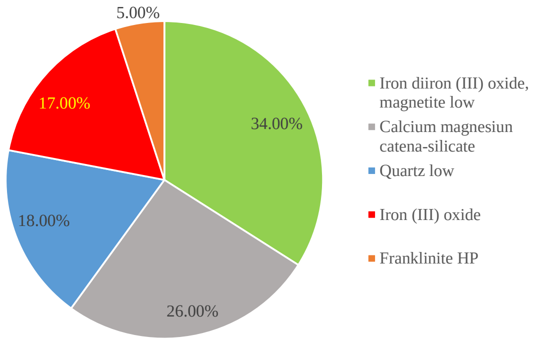

Fig. 1. Semi-quantitative percentage analysis of blast furnace slurries [5].

The sample’s chemical composition of the sludge and agglomerates samples was carried out by X-ray fluorescence elemental analysis (XRF) using the Brucker S8 Tiger type X-ray fluorescence spectrometer instrument operating a rhodium tube. The XRF analysis was performed after oxidation in air atmosphere (4 h at 950°C) and fusion fluxed with lithium tetraborate at 1200°C.
Mineralogical composition of the blast furnance sludge was determined using a Panalytical X'Pert PRO MPD diffractometer unit operating on Cu Kα radiation from the Ecometallurgical Research and Expertise Center, the University "Politehnica" Bucharest.
The morphology and composition of the sludge and agglomerate samples were studied using the technique of scanning electron microscopy (SEM) coupled with quantitative analysis by energy dispersive X-rays (EDX) with a Quanta Inspect F microscope, from the "Dunărea de Jos" University of Galați.

3. CHEMICAL COMPOSITION

The characteristics of sludge can be studied in order to understand and develop new techniques for pretreatment and separation of some metals [14]. Considering the literature survey and the results concerning the characterization of the bals furnance sludge from each plant is unique [15].
The initial stage for study of waste is the chemical characterisation of the waste, blast furnace dust in order to evaluate its suitability for use. In order to obtain agglomerate at the basicities imposed by the furnace coordinator or other producers, the furnace sludge must contain a significant percentage of iron, silicon, calcium and magnesium oxides [5, 9]. The indexing of the diffractogram obtained on the furnace sludge sample reveals 5 important chemical phases, in a large percentage of magnetite 34% being Fe_3O_4, calcium and magnesium silicate, $CaMgSi_2O_6$ in a percentage of 26%, and SiO_2 in a percentage of 18%, respectively hematite, Fe_2O_3 in a percentage of 17% (Table 1).

Table.1 Analysis of distinct phases in blast furnace dust

Chemical phase	Name	Crystal structure	2θ (max.)°	%
$CaMgSi_2O_6$	calcium and magnesium silicate	monoclinic	29.849°	26
SiO_2	silicon oxide	hexagonal	29.520°	18
Fe_2O_3	hematite	rhomboidal	33.146°	17
Fe_3O_4	magnetite	monoclinic	35.475°	34
$ZnFe_2O_4$	ferrous zinc oxide	cubic	35.530°	5

The chemical phases with iron are identified in difractogram with the positions at 2θ after 33, for hematite the position at 2θ at 33.146°, for magnetite the position at 2θ at 35.475° and ferrous zinc oxide the position at 2θ at 35.530° [15, 16].
In order to identify the elements in the composition, elemental analysis by X-ray fluorescence was performed both on the furnace slurry and on the sample of ferrous agglomerate resulting from sintering in the agglomeration machine (Table 2). Metallic elements are present in both types of samples, generally with changes in percentages in the chemical composition. Among the elements, iron is in greater quantity in the ferrous agglomerate (71.22%), otherwise also in the furnace sludge, being in a significant percentage, respectively 45.44% [17].
Calcium and silicon showed a slight decrease in the ferrous agglomerate compared to the furnace sludge, by 3.39% for calcium, respectively by 1.09% for their contribution in the complex sintering process.
Other identified elements such as Mg, Al, Mn, P, K, Ti, S, Cr and Cu, are in smaller quantities in the resulting ferrous agglomerate compared to the furnace sludge. It should be noted that the content of Zn and Cr, although they are in small percentage amounts, are about 10 times higher in the furnace slurry compared to the ferrous agglomerate, which suggests that the chemical elements are involved in the sintering process.

Table 2. The elemental composition of blast furnace slag and ferrous agglomerate

Chemical element	Blast furnace slag (%)	Ferrous agglomerate (%)
Fe	45.44	71.22
Ca	12.11	9.77
Si	6.24	5.15
Mg	2.28	1.79
Al	2.27	0.94
Mn	1.67	0.35
P	1.54	0.19
K	0.60	0.08
S	0.48	0.06
Ti	0.39	0.05
Zn	0.24	0.02
Cr	0.24	0.02
Cu	0.12	76 ppm

3.1. Mineralogical composition

An important stage in the analysis of the materials used for valorization is the mineralogical analysis [12, 13] The component elements of the raw and secondary materials used in the agglomeration/sintering process can combine into several minerals with different crystal structures that can interact with each other, preventing or enhancing the formation of new compounds [16, 17]. The components of blast furnace slurries are grouped into

different types of minerals, some can form carbonates (CaO and MgO), others require high temperature and pressure conditions (e.g. $CaMgSi_2O_6$ as well as various minerals that do not form carbonates following the process of melting/sintering (e.g. SiO_2). The main mineral phase in the blast furnace sludge was determined to be magnetite (34%), which is reasonable considering the iron content and the fact that mechanical dust formation from the iron burden generates magnetite and also hematite (17%) dust particles [14, 16].
The minerals present in the sludge and their distinctive behavior through the sintering process can be determined by X-ray diffraction (XRD) analysis, followed by quantitative mineral analysis [16, 17]. Running the XRD measurement in the diffractogram for sludge was observed between 20° and 30° (2θ), which is attributed to the amorphous coke. The diffractogram of this measurement is given in Figure 3. Different changes can be observed from a mineralogical point of view that occur as a result of the agglomeration process, important being the changes up to 50° (2θ) in particular (Figure 4) [18].

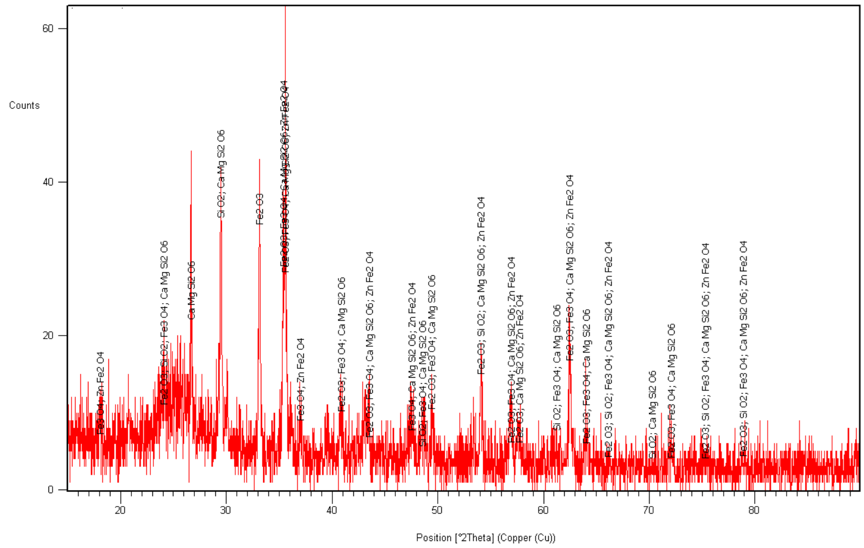

Fig. 3. X-ray diffractogram (XRD) of blast furnace sludge sample

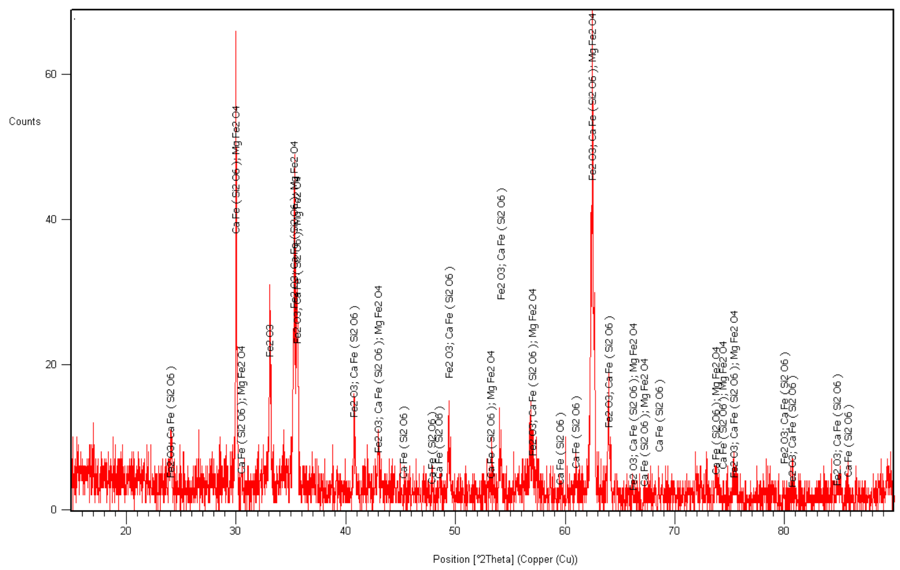

Fig. 4. X-ray diffractogram (XRD) of the agglomerate sample

If in the first zone, attributed to the amorphous state, SiO_2, the position at 2θ of 29.520°, as well as the calcium and magnesium silicate compound, $CaMgSi_2O_6$ at 2θ of 29.849°, iron and its compounds are also present, in the composition of the slurry of the furnace and a little bit in the agglomerate sample, at these positions. Comparatively, the X-ray diffractogram of the agglomerate obtained indicates complex structures in which the iron element is not absent even after 50° (2θ). There are details about the proportion of minerals that include iron and its oxides, with the large difference between the amounts of iron present in the ferrous agglomerate, compared to the furnace slag [17, 18].

3.2. Morfological characterization

The structural changes undergone by the materials subjected to different melting processes can be highlighted by morphological analysis using scanning electron microscopy (SEM) [11]. The blast furnace sludge samples and those resulting from the smelting process, respectively the ferrous agglomerate was examined without special prior preparation. SEM images were obtained at magnifications of 500X and 5000X, in order to have an overview of the component particles. Figure 5 shows the SEM images obtained on the blast furnace slag sample, as well as the spectra of the EDX analysis, related to the images, for the compositional confirmation of the metallic elements present in the sample (Figure 6).

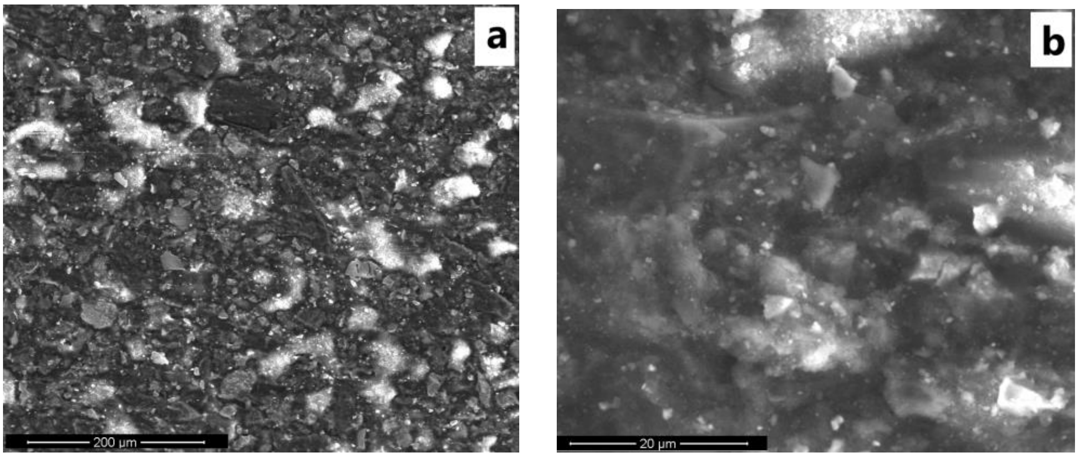

Fig. 5. SEM images regarding the morphology of the furnace sludge sample at 500X (a) and 5000X (b)

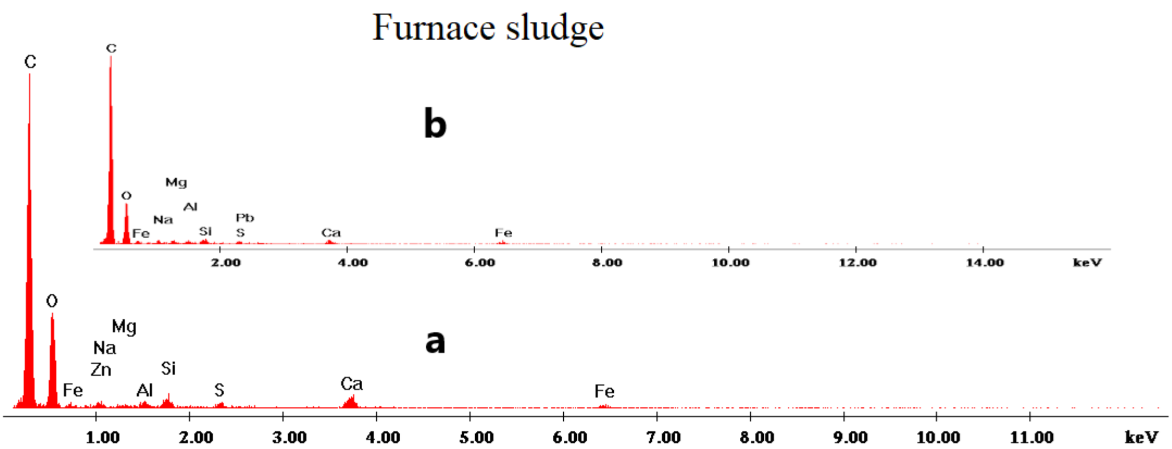

Fig. 6. EDX analysis of the furnace slam sample, from the SEM images (Fig. 5): a. 500X; b. 5000X

In Figure 7 shows the morphology of the ferrous agglomerate sample, which has a different appearance from the furnace sludge, obviously being a process of modifying the crystalline grains by melting. In the SEM-EDX study performed of sludge (Figure 5), Omran and Fabritius [10] associated zinc detected together with iron as franklinite. The larger iron oxide particle illustrated in Figure 7.b may be attributed also to franklinite with lesser zinc content, i.e., (Zn, Fe) Fe_2O_4. Also, the peaks of silica and calcium are overlapping suggesting that silica was present as well in the ferrous agglomerate (Figure 8).

Considering the distribution of iron and of other particles, the utilization of the sintering process the blast furnace sludge is of interest to study. The process introduces -particles interactions from the sludge and it has been shown to remove small particles attached to the surface of larger ones [9].

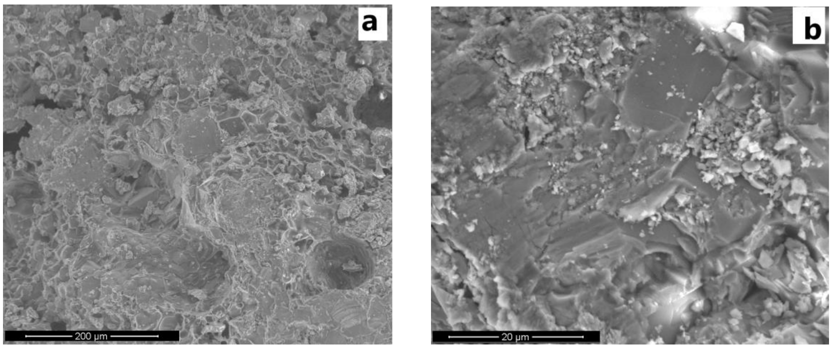

Fig. 7. SEM images regarding the morphology of the ferrous agglomerate sample:
a. 500X; b. 5000X

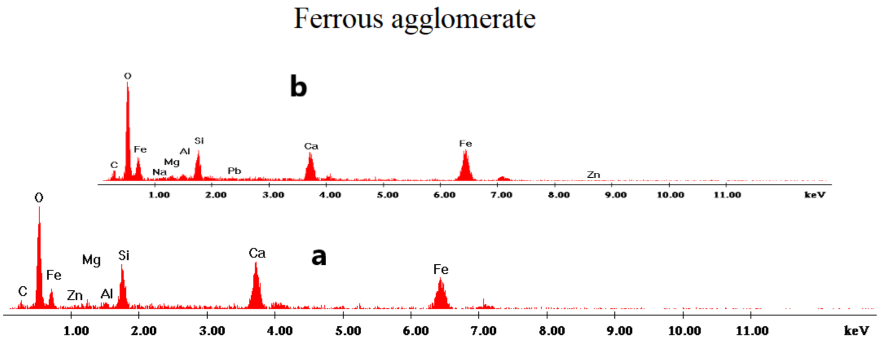

Fig. 8. EDX analysis of the ferrous agglomerate sample, from the SEM images (Fig. 5):
a. 500X; b. 5000X

From the comparative morphological analysis of the blast furnace sludge and the ferrous agglomerate, can be highlighted some aspects: the presence of major elements in both samples, for the different composition of the resulting complexes. For the content of carbon an obvious decrease was observed. The blast furnace sludge samples belong to the layer of very fine particles having the highest thermo-chemical activity in the melting process [18]. We can consider this characteristic as first phase of formation of the initial liquid melt that triggers the melt-solid reaction [19, 20]. The EDX analysis of the agglomerate sample (Figure 8) confirms the presence of iron in larger quantities, as well as silicon, calcium, and oxygen (in complex oxide structures) comparing with the analysis of the blast furnace sludge (Figure 6).

4. CONCLUSIONS

The furnace sludge and ferrous agglomerate samples were analyzed in order to to highlight the role and importance of distinct elements in the melting/sintering process. Five chemical phases are observed in the blast furnace dust, where the presence of silicon and calcium oxides leads to the formation of complex ferrites of calcium, aluminum and silicon during the sintering process from the sintering machine and contributes to the basicity index of the ferrous agglomerate.

The structural analysis confirms differences between the ferrous agglomerate sample and the blast furnace sludge sample with the contribution of SiO_2. This is dominantly found in the blast furnace sludge, and along with calcium in the agglomerate analysis, serve for the corresponding basicity. The obtained results confirm the usefulness of blast furnace sludge as a by-product in obtaining the ferrous agglomerate having iron with the largest contribution and silicon oxides.

The need to use the agglomeration process eliminates local pollution with sludge and dust during handling, by transforming the pulverulent waste into secondary products, to obtain the ferrous agglomerate and provides precise characteristics for this waste to be used in the agglomeration flow because it improves the chemical and structural spectrum of the charge of agglomeration and allows the manufacture of a higher quality agglomerate, with a higher iron content and good mechanical strength, [13].

The introduction of blast furnace slurries into the sintering process leads to increased iron content of the sintering stack and significant savings in iron-rich ores by reducing imports. At the same time, it reduces dust pollution and CO_2 emissions equivalent to reducing the consumption of powdered coke and electricity.

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