Solid Waste Management of a Chemical-Looping Combustion Plant using Cu-based Oxygen Carriers

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RECEIVED DATE.

ABSTRACT

Waste management generated from a Chemical-Looping Combustion (CLC) plant using copper based materials is analyzed by two ways: the recovery and recycling of the used material and the disposal of the waste. A copper recovery process coupled to the CLC plant is proposed to avoid the loss of active material generated by elutriation from the system. Solid residues obtained from a 10 kWth CLC prototype operated during 100 hours with a $\text{CuO-Al}_2\text{O}_3$ oxygen carrier prepared by impregnation were used as raw material in the recovery process. Recovering efficiencies of $\approx 80\%$ were obtained in the process, where the final products were an eluate of $\text{Cu}(\text{NO}_3)_2$ and a solid. The eluate was used for the preparation of new oxygen carriers by impregnation, which exhibited high reactivity for reduction and oxidation reactions as well as adequate physical and chemical properties to be used in a CLC plant. The proposed recovery process highly decreases the amount of natural resources (Cu and Al_2O_3) employed in a CLC power plant as well as the waste generated in the process. To determine the stability of the different solid streams during deposition in a landfill, these were characterized with respect to their leaching behavior according to the European Union normative. The solid residue finally obtained in the CLC plant coupled to the recovery process (composed by Al_2O_3 and CuAl_2O_4) can be classified as a stable non-reactive hazardous waste acceptable at landfills for non-hazardous wastes.

Keywords: Waste management, copper, leaching tests, CO_2 capture, Chemical-Looping Combustion.

1. Introduction.

According to the Intergovernmental Panel on Climate Change (IPCC), there is new and strong evidence that most of the warming effect observed over the past 50 years is attributable to human activities. Moreover, CO₂ emissions mostly due to fossil fuel combustion, are determining on the observed increase of the atmospheric CO₂ concentration during the 21st century. Recent scientific knowledge predicted that future anthropogenic carbon dioxide emissions will continue contributing to global warming and sea level rise for more than a millennium, due to the timescales required for removal of greenhouse gases from the atmosphere (1).

It is necessary therefore to enlarge the efforts to mitigate this impact as much as possible. One of the options for reducing net CO₂ emissions to the atmosphere includes capture and storage processes. Among the different technologies under development, Chemical-Looping Combustion (CLC) has been suggested as one of the most promising technologies for reducing the cost of CO₂ capture using fuel gas (2, 3).

CLC is a two-step gas combustion process that produces a pure CO₂ stream, ready for compression and sequestration. A solid oxygen carrier (OC) circulates between two reactors and transports oxygen from the combustion air to the fuel. Since the fuel is not mixed with air, the subsequent CO₂ separation process is not necessary. As gaseous fuel can be used natural gas or synthesis gas from coal gasification. In this system, the total amount of heat evolved from reactions in the two reactors is the same as for normal combustion, where the oxygen is in direct contact with fuel.

Since the process requires a good contact between gas and solids as well as a flow of solid material between the fuel and air reactors, the use of two interconnected fluidized beds have advantages over other designs (4, 5). The most common design of a CLC plant includes a high-velocity riser for the air reactor and a low-velocity fluidized bed for the fuel reactor, with the oxygen carrier in the form of metal oxide particles circulating between them (see Figure 1a). This layout is very similar to the commercial Circulating Fluidized Bed Combustors (CFBC's).

In the air reactor (AR), oxygen is transferred from the combustion air to the oxygen carrier. The exit gas stream from the AR contains N_2 and some unused O_2 . The particles carried away from the riser are recovered by a cyclone and fed to the fuel reactor (FR). In this reactor, the oxygen is transferred from the oxygen carrier to the gas fuel. The exit gas stream from the FR contains CO_2 and H_2O , and almost pure CO_2 is obtained after H_2O condensation. Finally, the particles are returned to the AR by gravity. Two particle seals prevent gas mixing between the two reactors. The technical risk of the system is therefore relatively low operating at atmospheric pressure because all the processes are carried out in standard process equipment and using elements of proven technology (4).

Figure 1. Schematic diagram of a CLC process coupled to a copper recovery and disposal processes.

Ideally, the number of reduction-oxidation cycles of the oxygen carrier in the system would be infinite. However, a makeup flow of new material (F_0) is necessary to compensate the loss of oxygen

carrier by elutriation (F_1 , F_2) as a consequence of particle attrition/fragmentation during the reduction/oxidation cycles. In some cases, the bed material smoothly loss their oxygen transport capacity and must be extracted from the bed (F_3) and renovated to keep constant the solids inventory into the system.

In economical terms the cost of this additional feeding is not significant to the overall cost of the plant, especially when using Cu-based materials (5). However, copper may be potentially supply limited, at least at low contemporary prices (6). Moreover, any new process needs the analysis of other important issues such as health and environmental impacts. According to Landner and Lindeström (7) copper is a potential toxicant at high levels. However, no works about waste management generated on this new combustion process can be found in literature.

The waste management should study the recovery and recycling of the used material and the disposal of the waste. Although the reuse of waste as material is of priority, the residual will still need to be deposited in a landfill. The most serious environmental impact of waste disposal to landfill is contamination of local groundwater by the generated leachate. In the European Union (EU) countries several tests have been developed to characterize and assess the constituents that can be released from waste materials. These tests are intended to identify the leaching properties of waste materials. Criteria and procedures for the acceptance of waste at landfills are established in the Council directive 1999/31/EC (8) and the Council decision 2003/33/EC (9) and all waste material must be sorted into one of three classes: hazardous, non-hazardous waste, and inert waste.

The objective of this work is to analyze several aspects related with the recovery and recycling of the material used in a CLC process as well as the characterization of the different solids materials before landing according to the EU normative. The work is centered in the material obtained in a 10 kWth CLC plant operated during 200 h with a Cu-based oxygen carrier prepared by impregnation on alumina (10, 11).

2. Experimental Section.

2.1 Impregnation method

The oxygen carriers used in this work were prepared by the dry impregnation method. The material was prepared by addition of a volume of a saturated copper nitrate solution (5.0 M) corresponding to the total pore volume of the support particles. Commercial γ -alumina particles (Puralox N_Wa-155, Sasol Germany GmbH) with a density of 1.3 g/cm³ and a porosity of 55.4 % were used as support. The chemical composition of the support was 95% min. Al₂O₃, 0.035% max. SiO₂, 0.025% max. Fe₂O₃, 0.005% max. Na₂O. Copper nitrate was provided by Panreac with an assay of 98% min. Other minor components were: Cl 0.005%, SO₄ 0.02%, As 0.0001%, Ca 0.05%, Fe 0.01, Mg 0.01%, Ni 0.05%, Pb 0.005%.

The aqueous solution was slowly added to the support particles, with thorough stirring at room temperature. The oxygen carrier was subsequently calcined for 30 min at 550 °C in a muffle oven to decompose the impregnated copper nitrates into insoluble copper oxide. Finally, the oxygen carrier was stabilized in air atmosphere for 1 hour at 850 °C. The final active CuO content was determined by TGA measurements. It must be considered that, for this type of Cu-based oxygen carriers, both the CuO and the copper aluminates are active species for reaction with the gas fuel (11).

2.2 Oxygen carrier characterization

Several techniques have been used to characterize the oxygen carrier particles. Reactivity tests and experiments to determine the oxygen transport capacity, Ro, of the oxygen carrier have been carried out in a thermogravimetric analyzer (TGA). Detailed information about the instrument and operating procedure used can be found elsewhere (12). Carrier porosity was measured by Hg intrusion in a Quantachrome PoreMaster 33. The identification of crystalline chemical species was carried out by powder X-ray diffraction (XRD) patterns acquired in an X-ray diffractometer Bruker AXS

D8ADVANCE using Ni-filtered Cu K α radiation equipped with a graphite monochromator. The copper distribution in a cross section of a particle embedded in resin epoxy was determined in a scanning electron microscope SEM Hitachi S-3400N, coupled to an EDX Rontec XFlash of Si(Li) detector for energy-dispersive X-ray (EDX) analysis.

2.3 Leaching behavior tests.

According to EU normative, the solid material obtained in a process must be characterized before disposal, and classified according to the European Council Decision 2003/33/EC (9). The characterization of CLC wastes was assessed by means of CEN 12457-3 leaching test (13), especially indicated for materials with high solid content and particle size below 4 mm. CEN 12457-3 is a two-stage batch leaching test performed at a cumulative liquid to solid (L/S) ratio of 10 l/kg (first leaching step, 6 hours at L/S=2 l/kg; second step, 18 hours at L/S=8 l/kg). In addition to the leaching limit values, granular wastes must meet the pH criteria.

The tests were carried out with several solid samples obtained from the operation of the CLC plant and after the copper recovery process (streams F₁, F₂, F₄ and F₅ in Figure 1). Batch tests involve mixing a sample of solid waste (~12.5 g) with distilled water (25 ml at L/S=2; 100 ml at L/S=8) in a polypropylene bottle. The mixture was agitated in a rotary agitation device at 10 r.p.m. during the leaching tests and after a contact time of 24 h, equilibrium conditions are assumed to have been reached. The mixture was later filtered to obtain the eluate. Two replicates samples were produced for each L/S fraction. Analyses for pH and metal content were carried out on these eluates. The later was carried out in an Inductive Coupled Plasma (ICP) Jobin Yvon 2000. pH was measured with microPH 2002 Crison immediately after the filtration steps included in the batch test.

3. Results and Discussion

Any new process for energy generation must be proposed according to sustainable development criteria. This includes the use of low amounts of natural resources, materials reusing, and safe disposal

of wastes. This work proposes a method to reuse the residues of a CLC plant by recovering the copper used in the process, and analyzes the safe disposal of the waste finally generated.

3.1 Waste characterization.

A Cu-based material (Cu14Al) prepared by impregnation on γ -Al₂O₃ with two different particle sizes (0.1-0.3 mm, 0.2-0.5 mm) was used as oxygen carrier in a 10 kWth CLC prototype. The prototype, composed of two interconnected bubbling fluidized bed reactors, was operated at 800 °C during 100 h for each particle size (10, 11). Table 1 shows the main characteristics of the oxygen carrier both fresh and after operation. The behavior of the oxygen carrier and the effect on methane conversion of different operating variables (oxygen carrier to fuel ratio, gas velocity, particle size, and temperature) were studied. The results obtained during continuous operation were very successful. Full conversion of CH₄ to CO₂ and H₂O was achieved in the FR using oxygen carrier-to-fuel ratios above 1.5. Moreover, this Cu-based material never presented agglomeration problems during operation. It must be remembered that this oxygen carrier was prepared according to manufacture conditions proposed by de Diego et al. (14) to prevent agglomeration.

The reactivity of the oxygen carrier particles hardly changed and it was maintained very high during operation. However, the CuO content of the oxygen carrier decreased during operation and therefore their oxygen transport capacity. Figure 2 shows the oxygen transport capacity of the oxygen carrier in reactivity tests carried out by TGA at 800 °C. The CuO content of the oxygen carrier particles have decreased up to 10 wt% (Cu14Al_{us}) at the end of the pilot plant test (100 h). The mechanism of CuO loss is not yet fully understood, although the loss rate was stabilized in a low value after the initial period of operation.

Figure 2. Reactivity of the oxygen carriers used in this work. 800 °C. $d_p=0.2-0.5$ mm. Reduction: 15% CH_4 + 20% H_2O . Oxidation in air.

With respect to attrition, the CuO loss was high at the beginning of the combustion test, but the rate decreased to $0.2 \text{ wt}\% \text{h}^{-1}$ after 40 h of operation, and to $\sim 0.04 \text{ wt}\% \text{h}^{-1}$ after 100 h. Fine oxygen carrier particles were mainly recovered downstream of AR (F_1 in Figure 1). The mass elutriated from FR (F_2 in Figure 1) was very much lower. However, both samples were enriched in CuO content, as it can be observed in Table 2.

Powder XRD patterns of the fresh oxygen carrier Cu14Al revealed the presence of CuAl_2O_4 and $\gamma\text{-Al}_2\text{O}_3$ as major crystalline phases and minor amounts of CuO. However, during operation $\gamma\text{-Al}_2\text{O}_3$ progressively evolved to $\alpha\text{-Al}_2\text{O}_3$ as a most stable phase at high temperatures (11). XRD analysis of the fines elutriated from each reactor showed that these streams had the same chemical compounds to the corresponding bed material. Therefore, some elemental Cu was detected in the FR outlet stream.

Table 1. Characteristics of the oxygen carriers. dp=0.2-0.5 mm.

Oxygen carrier	CLC operation		After Cu recovery process	
	Cu14Al	Cu14Al _{us}	Cu14Al _{rc} ^a	Cu14Al _{ri} ^b
Streams	F ₀	F ₃	F _{0,rc}	F _{0,ri}
Active material (%)	14	10	14	14
Ro (%)	2.7	1.8	2.7	2.7
Porosity	53.7	52.0	53.6	51.4
Average pore diameter (nm)	15	30	15	30
Apparent density (kg/m ³)	1560	1650	1550	1757
BET specific surface area (m ² /g)	77	32	77	29

^a prepared by impregnation of γ -Al₂O₃ as support using the eluate of the recovery process.

^b prepared by re-impregnation of the Cu14Al_{us} oxygen carrier using the eluate of the recovery process.

Table 2. Characterization of samples.

Stream	Sample	dp (μm)	CuO wt%	XRD Composition
CLC operation				
F ₀	Cu14Al	200-500	14	γ -Al ₂ O ₃ , CuAl ₂ O ₄ , CuO
F ₃	Cu14Al _{us}	200 – 500	10	γ -Al ₂ O ₃ , α -Al ₂ O ₃ , CuAl ₂ O ₄ , CuO
F ₁		< 40	60±10 ^a	γ -Al ₂ O ₃ , α -Al ₂ O ₃ , CuAl ₂ O ₄ , CuO
F ₂		< 40	44±5 ^a	γ -Al ₂ O ₃ , α -Al ₂ O ₃ , CuAl ₂ O ₄ , CuO, Cu
After Cu recovery process				
F _{0,ri}	Cu14Al _{ri}	200 – 500	14	γ -Al ₂ O ₃ , α -Al ₂ O ₃ , CuAl ₂ O ₄ , CuO
F _{0,rc}	Cu14Al _{rc}	200 – 500	14	γ -Al ₂ O ₃ , CuAl ₂ O ₄ , CuO
F ₅		<40	12 ± 4	γ -Al ₂ O ₃ , α -Al ₂ O ₃ , CuAl ₂ O ₄

^a Average value of samples obtained during 100 h operation.

3.2 Copper recovery process.

Since most of the fine particles ($< 40\ \mu\text{m}$) elutriated from the CLC plant corresponded to the AR, four samples with different CuO contents, corresponding to different operation times, were used for the copper recovery process. Figure 3 shows a scheme of the process. The samples were composed by $\gamma\text{-Al}_2\text{O}_3$, $\alpha\text{-Al}_2\text{O}_3$, CuAl_2O_4 and as above mentioned, were enriched in CuO. HNO_3 10 M was added to the solid sample at room temperature during 12 hours. After filtration, an eluate solution of $\text{Cu}(\text{NO}_3)_2$ and a solid material were obtained. The eluates were analyzed in an Inductive Coupled Plasma (ICP) Jobin Yvon 2000 to determine the amount of copper extracted in every recovery step. The test was repeated twice for each sample.

This solid residue was treated by two ways. By one way, it was dried overnight and stabilized by thermal treatment at $500\ ^\circ\text{C}$ in a muffle with air during 30 minutes to decompose the residual $\text{Cu}(\text{NO}_3)_2$ existing in the sample. By other way, the solid was thoroughly water washed and filtered (2nd recovery step). The low concentrate nitrate there obtained made necessary to include an additional concentration step to obtain a $\text{Cu}(\text{NO}_3)_2$ solution ready to be used for impregnation. The thermal stabilization after the first recovery process will produce nitrogen oxides which need to be take care of. The water-wash step will introduce more treatment stages in the recovery process and also waste water stream which needs a treatment process. The best option for an industrial recovery process will depend both on economic and environmental aspects.

Figure 4 shows the results obtained during the process. It can be observed that the copper recovery was very high in all cases, with an average value of 65% in the first recovery step and about 80% including both recovery steps. Moreover, XRD analysis showed that the solid sample obtained after thermal stabilization was mainly composed of CuAl_2O_4 . Two conclusions can be obtained from these analyses: 1) the process used is better acting in the CuO than in the aluminate phase, and 2) the CuO phase can be fully recovered from the sample.

Figure 3. Scheme of the copper recovery and disposal processes.

Figure 4. Summary of the copper recovery process from samples with different CuO content: initial, 1st recovery step, 2nd recovery step.

The $\text{Cu}(\text{NO}_3)_2$ solutions obtained after the recovery process were used to prepare by the dry impregnation method two new oxygen carriers with a 14 wt% of CuO: 1) $\text{Cu14Al}_{\text{rc}}$ ($F_{0,\text{rc}}$), using fresh alumina as support, and 2) $\text{Cu14Al}_{\text{ri}}$ ($F_{0,\text{ri}}$), produced by re-impregnation of the oxygen carrier $\text{Cu14Al}_{\text{us}}$ (F_3) used in the CLC prototype after 100 hours of operation.

These new oxygen carriers were characterized by several techniques to determine their behavior in a CLC process. The textural and structural properties of the oxygen carriers were studied by Hg porosimetry, N₂ physisorption, XRD and SEM-EDX. As seen in Table 1 and 2, the Cu14Al_{rc} oxygen carrier exhibited similar physical and chemical properties to the fresh Cu14Al oxygen carrier used in the prototype. The Cu14Al_{ri} oxygen carrier maintained similar characteristics to the Cu14Al_{us} used as raw material for the preparation of this sample.

Figure 5 shows the SEM images of the cross section of the fresh particles (Cu14Al), after operation in the CLC plant (Cu14Al_{us}), and after the re-impregnation process (Cu14Al_{ri}). The Cu14Al_{rc} exhibited a similar aspect to the Cu14Al oxygen carrier. The accumulation of small grains of CuO on the external surface of the fresh oxygen carrier (Cu14Al) is clearly revealed in Figure 5a. Most of these grains were separated from the particles by attrition and totally disappeared after 100 h of operation (Cu14Al_{us}), as it can be observed in Figure 5b. These fine particles were elutriated from the reactors and corresponded to the starter material used in the copper recovery process above mentioned. Moreover, SEM-EDX line profiles revealed that copper was uniformly distributed inside the particles, both in the fresh and reacted particles.

Figure 5. SEM photographs of the oxygen carriers. a) Cu14Al, b) Cu14Al_{us}, and c) Cu14Al_{ri}.

However, the Cu14Al_{ri} particles obtained by reimpregnation of the Cu14Al_{us} exhibited a CuO accumulation in some internal parts of the particles (Figure 5c), but did not showed any CuO layer in the external surface of the particles, as it happened during impregnation on fresh γ -Al₂O₃ (Cu14Al or Cu14Al_{rc}). This fact could be advantageous because could help to avoid the loss of copper during operation, as it happened with the fresh oxygen carrier prepared by impregnation on fresh γ -Al₂O₃, although more studies would be necessary to prove it.

However, it was necessary to know the behavior of these reimpregnated particles during the reduction and oxidation reactions. The reactivity of this material was determined by TGA and compared to the

original oxygen carrier used in the prototype (Cu14Al). A gas composed by 15 vol% CH₄ and 20 vol% H₂O for the reduction and pure air for the oxidation were used. As it can be observed in Figure 2, these new oxygen carriers (Cu14Al_{ri} and Cu14Al_{re}) exhibited similar oxygen transport capacity to the Cu14Al oxygen carrier. It is also remarkable the high reactivity, both in reduction and oxidation reactions, of all the oxygen carriers here presented with reaction times lower than 20 s to get conversion above 95%. This fact pointed out the good behavior of the reimpregnated particles which can be used without problems in a CLC process.

3.3 Leaching tests.

Several tests were carried out with the waste materials obtained during operation in the CLC plant (F1, F2 and F3 streams in Figure 1) to identify their leaching properties, and to know if they meet the waste acceptance criteria for landfill. The leaching tests have been focused only on copper since the raw materials used were analytical grade quality. According to the European Council Decision 2003/33/EC (9), the proposed limit values (PLV) for copper to be considered as a stable non-reactive hazardous waste acceptable at landfills for non-hazardous wastes are 25 mg/kg dry substance for L/S=2 l/kg and 50 mg/kg dry substance for L/S=10 l/kg. In addition to the leaching limit values, granular wastes must meet the pH criteria. The eluates must have pH values above 6. Table 3 shows the results of the batch tests carried out with the different wastes. It can be observed that all the streams obtained from the CLC plant could be deposited in the landfill without any problem, since the values obtained in the leaching tests are below the PLV.

Considering the CuO content of the elutriated streams, a process to recover this copper has been proposed in this work. To be sure that this process will not generate new environmental problems, other leaching tests were carried with samples obtained from this process. It can be observed in Table 3 that solids obtained in the first copper recovery step, before stabilization stage, (stream F4 in Figure 1) exceeded the PLV and pH criteria and could not be deposited in a landfill. However, the samples stabilized after an easy thermal treatment (stream F5 in Figure 1) exhibited acceptable leaching

properties. This was not strange considering that these samples are composed by copper aluminates and inert Al_2O_3 .

Table 3. Leaching properties of the different CLC waste streams and average values of pH. PLV=25 mg Cu/kg dry matter for L/S=2, and PLV=50 mg Cu/kg dry matter for L/S=10. Minimum limit value for pH = 6.

Stream	pH	L/S=2 L/kg (mg Cu/kg dry matter)	L/S=10 L/kg (mg Cu/kg dry matter)
F ₃	6	3	15
F ₁	6	3	3
F ₂	6	3	15
F ₄ (F ₁) ^a	4	1000	1399
F ₄ (F ₂) ^b	5	1042	1986
F ₅ (F ₁) ^a	6	3	13
F ₅ (F ₂) ^b	6	3	13

a) Solid residue when use F₁ in the copper recovery process.

b) Solid residue when use F₂ in the copper recovery process.

3.4 Copper Mass balance in a CLC Power Plant.

To remark the consequences of the recovery process proposed in this work, a mass balance focused on copper corresponding to a 100 MWth CLC power plant was done (see Table 4). The solids inventory necessary for the CLC process operating with the Cu-based oxygen carrier was calculated from a mass balance of the solid and gas in the fuel and air reactors (5). For preliminary calculations, it was assumed perfect mixing of the solids, gas plug flow in the beds, and no resistance to the gas exchange between the bubble and emulsion phases. The lifetime of the particles was calculated from the attrition rate experimentally obtained during the 100 h of operation in the 10 kWth CLC prototype (10, 11). According to those values, the renovation of the solids must be carried out about three times a year. It

must be considered that the rate of copper use has risen rapidly in recent decades, especially in the metal industry. It is obvious that this usage trend cannot be sustained indefinitely at least at low contemporary prices, especially because copper's depletion time (reserves/annual use) is no more than 30-50 years. This situation suggests the desirability of extensive reuse of copper in use (15).

Table 4. Copper mass balance in a CLC power plant.

	Without copper recovery	With copper recovery	
		with fresh alumina	re-impregnation
Oxygen carrier	Cu14Al	Cu14Al _{rc}	Cu14Al _{ri}
Power (MWth)	100	100	100
Solids inventory (kg OC) ^a	15000	15000	15000
Attrition rate (wt% / h) ^b	0.04	0.04	0.04
Lifetime (h) ^b	2400	2400	2400
Makeup flow - F6 - (kg/year)			
CuO	6300	1260	1260
Al ₂ O ₃	38700	38700	7740
OC Waste (kg/year)	45000	39960	9000

a From ref. (5).

b From refs. (10) (11).

For comparison reasons, another mass balance was done considering the copper recovering process coupled to the CLC plant. It can be observed that this process reduce a lot the use of starter material, mainly copper and Al₂O₃, as well as the amount of OC waste produced. The numbers here presented point out the importance of the copper recovery process because it reduces the copper resources necessities and produces a stream composed by Al₂O₃ and CuAl₂O₄, which can be classified as a non-hazardous waste according to the EU normative. This waste can be deposited in a landfill in a safe way.

It must be considered that this recovery process has been centered in the use of oxygen carriers based on copper and prepared by impregnation. More studies will be necessary to extend this process to other metals (Ni, Fe, etc.) or preparation methods (spray drying, etc.).

ACKNOWLEDGMENT

This research was carried out with financial support from the Spanish Ministry of Education and Science (Projects PPQ-2001-2111, CTQ-2004-04034) and from the Diputación General de Aragón (Project PIP023/2005). C. R. Forero thanks UNIZAR-BSCH for the predoctoral fellowship.

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