Magnetite Dissolution by Copper Catalyzed Reductive Decontamination
촉매제로 구리이온을 이용한 환원성 제염에 의한 마그네타이트 용해

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Hydrazine based reductive dissolution applied on magnetite oxide was investigated. Dissolution of Fe(Ⅱ) and Fe(Ⅲ) from magnetite takes place either by protonation, surface complexation, or reduction. Solution containing hydrazine and sulfuric acid provides hydrogen to break bonds between Fe and oxygen by protonation and electrons for the reduction of insoluble Fe(Ⅲ) to soluble Fe(Ⅱ) in acidic solution of pH 3. In terms of dissolution rate, numerous transition metal ions were examined and Cu(Ⅱ) ion was found to be the most effective to speed up the dissolution. During the cycle of Cu(I) ions to Cu(Ⅱ) ions, the released electron promoted the reduction of Fe(Ⅲ) and Cu(Ⅱ) ions returned to Cu(I) ion due to the oxidation of hydrazine. In the experimental results, the addition of a very low amount of cupric ion (about 0.5 mM) to the solution increased the dissolution rate about 40% on average and up to 70% for certain specific conditions. It is confirmed that even though the coordination structure of copper ions with hydrazine is not clear, the Cu(Ⅱ)/H+/N2H4 system is acceptable regarding the dissolution performance as a decontamination reagent.

Keywords: Decontamination, Reductive dissolution, Metal oxide, Reactor coolant system, Waste reduction, Catalytic effect

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본 연구에서는 하이드라진 기조의 환원성 제염제를 이용한 마그네타이트 산화물의 용해를 다루고 있다. 마그네타이트로부터의 Fe(Ⅱ) 및 Fe(Ⅲ)의 용해는 protonation, surface complexation 및 reduction에 의해 지배를 받는다. 하이드라진과 황산은 산소결합을 파괴하거나 Fe(Ⅲ)이온을 Fe(Ⅱ)이온으로 환원시키기 위한 수소 및 전자를 각각 제공하게 된다. 속도론적 관점에서 보다 효율적인 용해를 위하여 다수의 전이금속의 영향을 분석하여 Cu(Ⅱ) 이온이 효과적임을 확인한 바 있다. Cu(Ⅰ) 이온은 Cu(Ⅱ) 이온으로 산화되는 동안 전자를 방출하여 Fe(Ⅲ) 이온을 환원시키고 다시 하이드라진에 의해 Cu(Ⅰ) 이온으로 환원되게 된다. 본 연구를 통해 제염용액에 매우 적은 양의 구리 이온 (약 0.5 mM)을 첨가함에 따라 평균 40% 용해속도가 향상됨을 확인하였고, 특히 특정 조건에서는 70% 이상 용해속도가 향상 됨을 확인하였다. 구리 이온이 하이드라진과 배위결합을 이루는 지에 대해서는 아직 명확하지 않으나, 분명한 것은 Cu(Ⅱ)/H⁺/ N₂H₄으로 이루어진 제염제는 효과적인 용해성능을 가지고 있다는 것이다.

중심단어: 제염, 환원용해, 금속산화물, 원자로냉각재계통, 폐기물 저감, 촉매 효과

1. Introduction

Of numerous metal oxides, magnetite is the one of the major corrosion products found in many nuclear power plants. Magnetite formed under high temperature (greater than 270℃) and pressure (around 16 MPa) which is the normal operating condition of reactor coolant system is intrinsically very inert and additionally contains radioactive isotopes such as ^{60}Co or ^{58}Co which are necessarily removed to reduce the occupational radioactive exposure [1]. Chemical decontamination accompanying dissolution of oxide layers by chemical solutions remains a viable option for nuclear power plants to reduce the radioactive exposure and still organic acids are widely used as a strong decontamination reagent due to the faster dissolution rate and chelating capacity.

Dissolution of metal oxides in aqueous acidic solutions is primarily controlled by the protonation of metal-oxygen bonding to release the metal ions from the oxide lattices but in the presence of reducing or chelating agents dissolution is often facilitated by the enhanced mass transfer of metal ions together with chelating reagents as well as metal reduction to soluble state such as insoluble ferric ions to soluble ferrous ions of hematite. Magnetite contains both bivalent iron (Fe(Ⅱ), Fe^{2+}, or ferrous ion) and trivalent iron (Fe(Ⅲ), Fe^{3+}, or ferric iron) and relatively faster dissolution rate because instable ferrous ions existing in the lattice of oxide could be released easily to the solution requiring short induction period. Therefore, Fe(Ⅲ) to Fe(Ⅱ) is thought to decrease the strength of the bond of Fe to the underlying lattice in iron oxide. The dissolution of Fe-containing oxide is slower by oxidative condition than reductive condition.

The mechanisms and kinetics related to the metal oxides dissolution in varied acidic reagents have been reported for many decades even though a general picture of dissolution is not available due to the peculiarity of each oxide in structure, stability of metal ions, solubility, and reactivity. In a number of experimental results and practical reports, organic acids such as oxalic acid [2-8], citric acid [9-12], ascorbic acid [10, 11, 13-16], malonic acid [17-19], thioglycolic acid [20-22], etc. were used as solvent reagents and many other literatures reported the effectiveness of the chelating agents in dissolution rate such as imino-diacetic-acid (IDA) [23, 24], N-hydroxyethy-imino-diacetic-acid (HIDA) [23], diethylene-triamine-pentaacetic-acid (DTPA) [25], nitrile-triacetic-acid (NTA) [26], and ethylene-diamine-tetraacetc-acid (EDTA) [8, 11, 23, 25, 27-31] by the sorption of dissolved metal ions forming stable metal chelates. Also reductive dissolution by the addition of reducing reagents such as hydrazine [9, 32], vanadium [30] as well

as organic acids were reported with effective experimental results.

However, organic acids and chelating ligands are often problematic on the safety of radioactive wastes. Organic compounds in a repository potentially form a complex with radionuclides, which increases the mobility of radionuclides and consequently increases the probability of the radioactive contamination of groundwater [33]. Furthermore oxalic acid can cause a severe intergranular attack (IGA) to the type 304 stainless steel [34]. Therefore, the use of organic acids or chelating reagents even though those effects to the dissolution performance is much greater than other chemical components must be minimized or carefully determined with appropriate treatment processes. Alternatively dissolution accommodated by inorganic reducing reagents or catalysts in inorganic acid solutions have been extensively studied for the feasible dissolution outcomes. The experiments of Kumar et al. [35], in which the dissolution between synthetic nickel and cobalt doped goethite and pure goethite was compared, used the mixtures of sulfuric acid and sulfurous acids as a dissolution media due to the effect of protonation by H_2SO_4 and reducing effect of H_2SO_3. The increased dissolution of magnetite was also found in the studies of Senanayake and Das [36]. They used copper ions in the sulfur dioxide solution similar to the studies of Byerley et al. [37]. In those studies, SO_2 was used as a reducing catalyst to form $FeHSO_3^+$ with Fe(III) from iron oxides and accordingly the concentration of Fe(III) ions decreases to accelerate the iron oxide dissolution.

The present study is concerned with the feasibility of not using the organic compounds for the dissolution of oxide layers. We propose an acidic solution containing sulfuric acid, hydrazine, and copper ions for the effective dissolution of magnetite powders magnetite powders which are considered as a representative oxide form found in reactor coolant system. The effects of both hydrazine and copper ions as a reducing agent and a catalyst respectively to promote the reducing power, as well as temperature will be investigated on the dissolution of magnetite powder.

2. Experimental

2.1 Magnetite and Dissolution Agents

Magnetite nanopowders (Fe_3O_4, Junsei chemical, >99 %) were put in 250 ml Nalgene polypropylene (pp) bottles for the dissolution and 50 ml conical tubes for the screening test. Nitric acid (HNO_3, Reagent & Chemicals, extra pure reagent) and sulfuric acid (H_2SO_4, Showa, guaranteed reagent) were used to adjust the acidity for screening test and dissolution test respectively. Hydrazine monohydrate ($N_2H_4 \cdot H_2O$, 80%, Junsei chemical, extra pure reagent) was used as a reducing agent with the concentration range of 10 to 100 mM. Screening tests to check the catalytic effect were conducted for the following transition metal ions; Co(II), Ni(I), Cu(II), Zn(II), Ru(III), Rh(III), Pd(II), Ag(I), Cd(II), Ir(III), and Pt(II).

2.2 Dissolution Procedures

2.2.1 Screening test for the selection of dissolution effective transitional metal. In screening tests of transitional metal ions, each 40 ml solution contains 4 mg of metal ions (100 ppm), 70 mM N_2H_4 and 5 mg of magnetite at pH 3 adjusted by HNO_3. All tests were in 50 ml conical tubes with shaking in water bath at 90℃ for 3 hours. The dissolved amount of magnetite was measured with a flame atomic absorption spectrophotometer of the Perkin Elmer's.

2.2.2 Dissolution tests. The solutions for dissolution tests were prepared in a magnetically stirred 250 ml Nalgen polypropylene (pp) bottle at a room temperature. Hydrazine monohydrate in concentrations from 0 to 100 mM (equivalent to 1.23 ml in total 200 ml distilled solution) was added and then the pH of the solution was adjusted from 1 to 4 with sulfuric acid. Copper(II) sulfates ($CuSO_4$, 97.5%, Kanto chemical Co., Japan) with the amount from 0 to 0.033 g were put in the solution. After fully mixed, the solution

Table 1. Experimental conditions of Magnetite Dissolution

Experiments	N_2H_4 [mM]	$CuSO_4$ [mM]	pH	Temp. [℃]	Fe_3O_4 [ppm]	Duration [h]
Transition metal screening exp.	70	-	3	90	71.4	3
N_2H_4 effect exp.	0 - 100	0 0.5	3	95	35.8	20
Cu^{2+} effect exp.	0 - 100	0 - 1	3	95	35.8	20
Temp. effect exp.	50	0 - 2	3	75 - 95	35.8	2

was kept in water-bath with shaking for the experiments of different dissolution temperatures (75, 85, and 95℃). After 1 hour when the temperature of the solution was reached to the designated temperature, the dissolution tests were initiated with the addition of 0.01 g of magnetite. The amount of magnetite used in this study was 3 to 5 folds excessive compared to the amount of that observed in the surface of reactor coolant systems. All solutions were closed tightly and periodic sampling was carried out with a syringe and then filtered through a 0.2 μm pore membrane. All samples were stored under oxygen-free N_2 conditioned until the atomic adsorption spectroscopy (AAS) analysis. The summarized experimental conditions were listed in Table 1.

Fig. 1. Dissolved fraction of Fe_3O_4 with different concentration of N_2H_4.

3. Results and Discussion

3.1 Hydrazine and Hydrogen Sulfate System

Fig. 1 gives the dissolved fraction of magnetite at different values of hydrazine concentration. The observance of dissolution in only 0.1 M H_2SO_4 system equivalent to pH 1 was also included in the figure for the comparison of dissolution efficiency. From the results, we found no practical dissolution of magnetite in the absence of hydrazine at pH 3. On the other hand, the dissolved fraction of magnetite increased proportional to the concentration of hydrazine.

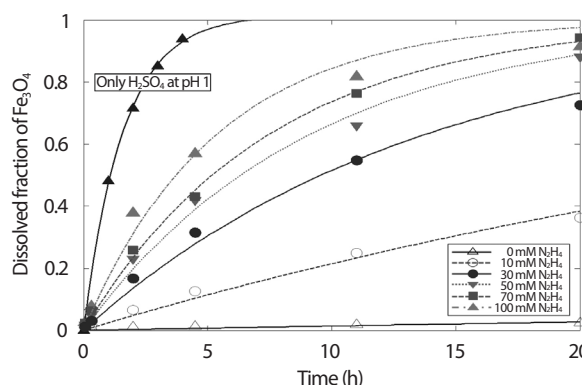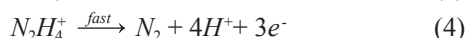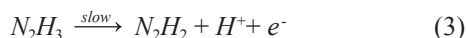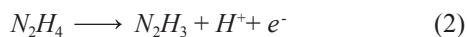To study the effect of hydrazine, the dominant species of

hydrazine in acidic solution is hydrazinium ion, $N_2H_5^+$. The equilibrium constant in Equation (1) is the order of about 10^{-8} - 10^{-9} from literature [38]. Oxidation of hydrazinium ion and further to nitrogen in the solution where a reduction half-cell reaction presents is described in Equations (1) to (4). Reactions by 1 or 2 electron transfer from hydrazinium are known relatively slow and limiting overall reaction rate, which corresponds that further electron transfers proceed faster [39, 40].

$$N_2H_5^+ \rightleftharpoons N_2H_4 + H^+ \qquad (1)$$
$$N_2H_4 \longrightarrow N_2H_3 + H^+ + e^- \qquad (2)$$
$$N_2H_3 \xrightarrow{slow} N_2H_2 + H^+ + e^- \qquad (3)$$
$$N_2H_4^+ \xrightarrow{fast} N_2 + 4H^+ + 3e^- \qquad (4)$$

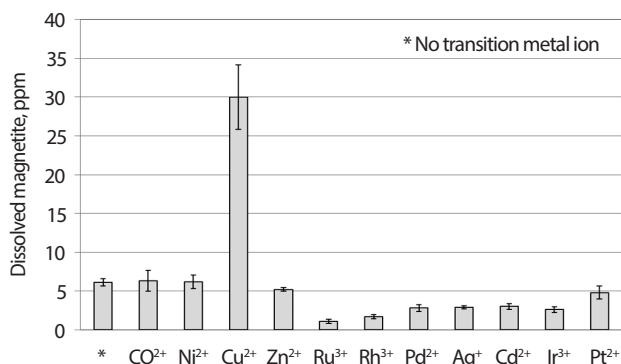Compared to the result of the dissolution in only acidic

Fig. 2. The effect of transition metal ions (100 ppm [$M^{+/2+/3+}$] respectively) for the dissolution of magnetite. A significant promotion of magnetite dissolution was observed only by the addition of cupric ions (at 70 mM N_2H_4, pH 3, 90℃ for 3 hours, [Fe_3O_4] $_{max}$= 71 ppm).
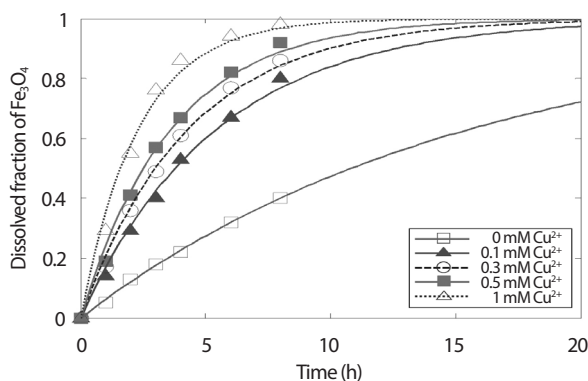

Fig. 3. Dissolved fraction of Fe_3O_4 with different concentration of Cu(Ⅱ) ions (solutions of 20 mM N_2H_4 + x mM Cu(Ⅱ), where x = 0, 0.1, 0.3, 0.5, and 1 at pH 3, 95℃).
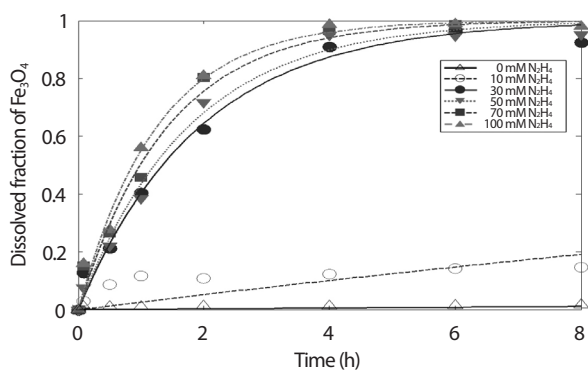

Fig. 4. Dissolved fraction of Fe_3O_4 with different concentration of N_2H_4 with the presence of cupric ions (solutions of 0.5 mM Cu(Ⅱ) + x mM N_2H_4, where x = 0, 10, 30, 50, 70 and 100 at pH 3, 95℃).

solution by H_2SO_4, however, the amount of dissolved magnetite in 100 mM hydrazine solution accounts for 70% of that and it can be deduced that the dissolution by only hydrazine solution in the magnetite dissolution is not much significant to overwhelm the dissolutive performance by the acidic solution.

3.2 Screening of Transitional Metal Ion Catalysts

The foregoing screening tests have shown that the dissolution of magnetite can be accommodated by the effect of dissolved metal ions. The results show that the existence of metal ions especially Cu(Ⅱ) in the acidic solution containing 70 mM hydrazine accelerated the dissolution of magnetite in 3 hours as shown in Fig. 2. In the system studied, some metal ions such as Ru^{3+}, Rh^{3+}, Ir^{3+}, Pd^{2+}, etc. rather hindered the dissolution efficiency. The study of the effect by the Cu(Ⅱ) ion will be discussed in the following section.

3.3 The Effect of Cu(II) Addition

Based on the studies for the effect of transitional metal ions, we have chosen the Cu(Ⅱ) ions for the dissolution of magnetite. Fig. 3 shows the dissolved fraction of magnetite in varied concentrations of Cu(Ⅱ) ions. The higher concentration of the copper ion is in the solution, the faster dissolution rate of the magnetite was observed. With no presence of Cu(Ⅱ) ions, the fraction of dissolved magnetite was about 70% in 20 hours, but in the presence of Cu(Ⅱ) ions could increase the dissolved fraction of magnetite by 90% in 6 hours and 100% in 10 hours.

We also performed the dissolution tests at the same conditions shown in Fig. 1 only with different condition of Cu(Ⅱ) addition. Compared to the dissolution result with no addition of Cu(Ⅱ) ions in Fig. 1, the addition of a small amount of Cu(Ⅱ) ions drastically increased the dissolution rate as shown in Fig. 4.

The acceleration of dissolution in the presence of Cu(Ⅱ) ions can be explained that Cu(Ⅰ) ions reduced from
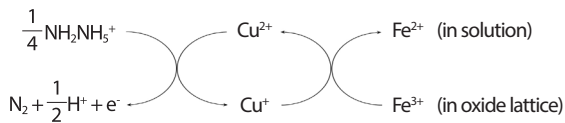
Fig. 5. Reduction mechanism of ferrous ions by the mixture of hydrazine and cupric ions. Ample N_2H_4 reduces cupric ions to cuprous ions in the bulk solution.
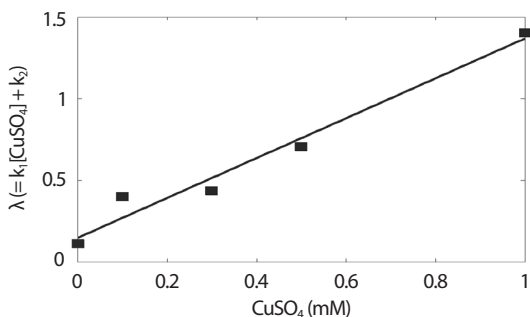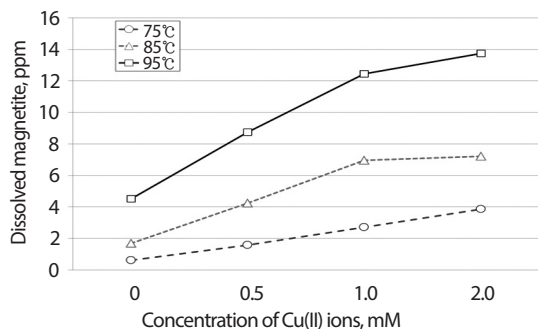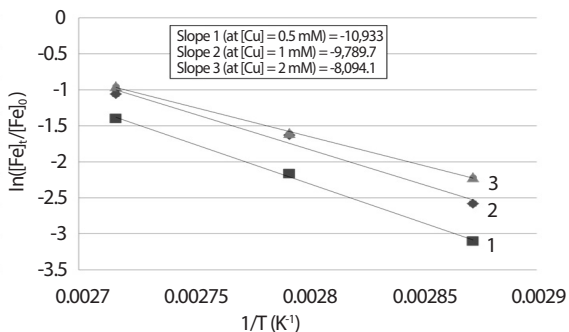

Fig. 6. The relationship between concentrations of cupric ion added in solution and λ of Equation (5).

(a)

(b)

Fig. 7. (a) Dissolved amount of Fe_3O_4 in temperatures from 75 to 95℃ (at $[N_2H_4]$ = 50 mM, pH 3, $[Fe_3O_4]_{max}$ = 35.8 ppm, $[Cu^{2+}]$ = 0, 0.5, 1 and 2 mM), and (b) slope for the calculation of activation energy (slope = -Ea/R).

Cu(II) ions by the oxidation of hydrazine play a role of reducing Fe(III) ions into soluble Fe(II) ions as shown in Fig. 5. Simultaneously hydrogen ion and electron produced by the oxidation of hydrazine are thought to increase the dissolution rate.

Another mechanism is also available to describe the interaction between Cu(II) ions and hydrazine. Cu(II) ions in acidic solution may form a coordination complex which is expected in the formation of $[Cu^+(N_2H_4)]$, $[Cu^+(N_2H_5^+)]$, or $[Cu^+(N_2H_5^+)(SO_4)^{2-}]$. The bridged bond between Cu(I) ion and hydrazine could communicate to transfer an electron from Cu(I)ion to Fe(III) of magnetite. It also supports that the reduction of Cu(II) ions, which was oxidized by the reaction with Fe(III), to Cu(I) is effective in the further oxidation of hydrazine. A close examination for coordination compounds and the reaction pathway is required but beyond the scope of the current study. To quantify the effect of a cupric ion on the total dissolution rate, we examined the relationship between the concentration of a cupric ion and the reaction rate from the regressive profile of magnetite dissolution in an acidic solution approximated as a function of time (Equation (5)),

$$C(t) = C_0(1-e^{-\lambda t}) \tag{5}$$

where C_0 is the initial Fe concentration in magnetite, and is a concentration achievable by complete dissolution and $C(t)$ is the concentration dissolved in a solution at time t. In general, λ is a parameter dependent on the experimental conditions such as temperature, concentration of the reactant or solutes, and acidity. This empirical regression model has already been fitted to the magnetite dissolution, as shown in Fig. 3. The relationship between the concentration of cupric ion added in the solution and λ of Equation (5) was plotted in Fig. 6.

Values of λ were estimated by a least squares method using the data obtained from the experiments. As shown in the figure, it was found that the coefficient λ is proportional to the concentration of cupric ion added in the solution.

This result supports the proposed catalytic effect of copper ions between the oxidation of hydrazine and reduction of ferric ions.

3.4 Effect of temperature

To study the effect of temperature on magnetite dissolution, tests were conducted at 75, 85 and 95℃ at a constant pH of 3, and 50 mM N_2H_4 and varied Cu ion concentrations for 2 hours. Plots of dissolved magnetite versus temperature are presented in Fig. 7(a). As the temperature increased, the rate of dissolution also increased. For every 10 celcius degree increase in temperature, the reaction rate was almost doubled. From the result, the values of activation energy were calculated as 90.9, 81.3, and 67.3 kJ·mole^{-1} for the addition of 0.5, 1, and 2 mM Cu(Ⅱ) ions respectively as shown in Fig. 7(b), which means that the dissolution rate is highly dependent on the temperature. This result also confirmed the catalytic effect of Cu(Ⅱ) ions to lower the activation energy.

4. Conclusions

The results of this study have shown that the dissolution of magnetite by the mixed system of sulfuric acid, hydrazine, and Cu(Ⅱ) ions strongly depends on the reducing effect by hydrazine and catalytic effect of Cu(Ⅱ) ions. Acid primarily supplies protons to break Fe-O bond and hydrazine plays a reducing reagent role to dissolve the Fe(Ⅲ) ions into the solution. Cu(Ⅱ) ions assumed to form a bridge bond with hydrazine promoted the dissolution by decreasing activation energy. Also Cu(Ⅱ) ions decompose the hydrazine generating protons and electrons and Cu(Ⅰ) ions are again oxidized by dissolving Fe(Ⅲ) ions. From the reasons above, the addition of 0.5 mM Cu(Ⅱ) ions in the acidic solution containing 50 mM hydrazine increased the dissolution fraction from 38% to 89% at 4 hours. Although we have used some detailed numbers of dissolution rate in this paper, those are only from the dissolution experiments of magnetite, the surrogate test. Therefore the data shown everywhere in this paper do not directly mean the actual performance. While it needs a close examination whether the proposed mechanism is acceptable, it is clear that proposed dissolution system is feasible since the most decontamination process practically takes 10 to 12 hours in the reduction step.

Acknowledgments

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