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# Application of biosurfactants for the mineral surfaces modification

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Modification of surface properties of various minerals can be a key for the mineral separation. Biomodification of the mineral properties was realised by the adsorption of biosurfactants, which were produced by Pseudomonas aeruginosa. In this study, it is shown that Pseudomonas can grow in the presence of minerals and produce a biosurfactant with substantially changes of the surface tension of supernatant. Measurements confirmed that an interaction of all used minerals with the supernatant caused a decrease of zeta potential. As expected, the ieps of mineral particles were shifted to lower pH values after the interaction with biosurfactant. Bio-pretreatment of the minerals has affected on the settling properties of mineral suspension. The settling results showed a strong flocculation for investigated suspensions at the present of the small biosurfactant concentration (2 % v/v).

## 1. INTRODUCTION

The problem of solid surface bio-modification is still an open issue despite some attempts to solve it. During the past decade the mineral beneficiation realised by chemoautotrophic bacteria is the most widely applied process for copper and gold recovery [1,2].

Biosurfactants are mainly produced in aqueous media from the carbon sources by growing microorganisms. Their use has been restricted to specific application. Commercially they are used as emulsifier reagent for hydrocarbon [3]. Many microorganisms produce effective biosurfactants which reduce the interface tension between oil and brine to less than 0.01 mN/m. Biosurfactants are easily biodegradable and are particularly suited for bioremediation of oil dispersion. The biosurfactants affect the rate of hydrocarbon biodegradation in two ways: by increasing solubilization and by changing the affinity between microbial cells and hydrocarbon [4].

Removal of entrapped organic liquid (hexadecane) can be enhanced by the use of bio-surfactants. The in situ biodegradation of entrapped contaminants by rhamnolipid biosurfactant was investigated [5,6].

A detailed understanding of the biosurfactant role in modification of the mineral surface is currently lacking. The aim of the work described in this paper is to investigate how biosurfactants produced by Pseudomonas aeruginosa affect the behaviour of mineral suspensions.

## 2. MATRIALS AND METHODS

### 2.1. Microorganism

The bacterial strain used in our experiments was *Pseudomonas aeruginosa* isolated from the soil samples. Cells were grown in 250 ml Erlenmeyer flasks containing 50 ml of liquid medium. Growth experiments were carried out with the medium consisted: 20 g/l mannitole, 0.05 M $NH_4NO_3$, 0.03 M $KH_2PO_4$, 0.04 M $Na_2HPO_4$ $7H_2O$, 8 $10^{-4}$ M $MgSO_4$, 7 $10^{-6}$ M $CaCl_2$, 4 $10^{-6}$ M $Na_2EDTA$, 10 mg/l $FeSO_4$ 7 $H_2O$. The chemicals were used as received without further purification. The strain was cultured in a rotary shaker (100 rpm) at the room temperature. The samples were taken every day, centrifuged (4000rpm at 10 min.) and the supernatants were used for surface tension measurements. The bio-surfactants synthesized by *P. aeruginosa* are most probably a mixture of rhamnolipids and glycolipids. The mineral sample (2 g) was added to the medium before sterilisation. The number of living cells in the cultures was determined by the standard colony counting method.

### 2.2. Minerals

In this study, the pure mineral samples of hematite, kaolin, dolomite and chalk (calcite) were used. Kaolin was supplied by Surmin-Kaolin mine (AKW Group) (Poland). The average particle diameter was 1.1 μm. Hematite was purchased from Ward's Natural Science Rochester, NY. (USA) and was ground to the size -40 μm in a laboratory mill. Dolomite and chalk powders with the particle size specifications given as 90 w% < 40 μm were supplied by the Department of Geology University of Wroclaw (Poland).

### 2.3. Surface tension measurements

Surface tension measurements were carried out by the ring method with a K10T tensiometer (Kruss, Germany). Surface tension measurement is a common tool to monitor the growth of microbial culture. Each value represents the mean of five measurements. All glassware was cleaned in chromic acid and washed in Mili-Q water.

### 2.4. Adsorption measurements

In the experiment for the biosurfactant adsorption, 2 g of mineral was added to the biosurfactant solution. The concentration of biosurfactant solution was changed from 1 to 0.1 of an initial concentration. After 12 hours equilibration, the surface tension of supernatant was measured. From the difference of the surface tensions between the initial solution and the equilibrium solution, the adsorption has been calculated.

### 2.5. Zeta potential measurements

Electrophoretic measurements were carried out with a particle micro-electrophoresis Nicomp™ 380 ZLS apparatus (Santa Barbara, California, USA). Measurements were made for diluted suspensions, obtained by adding a small quantity of mineral particles to the solution. The ionic strength of dilute suspensions was maintained at $10^{-3}$ M using NaCl. The samples were ultrasonicated for 2 min before measurements.

### 2.6. Sedimentation experiments

The mineral suspensions were prepared by adding 2-gram mineral samples to the Andreasen pipette. Agitation and pH conditions were the same as for the biosurfactant free suspensions. The stability of mineral suspension was calculated from the relationship:

$$Stability(\%) = \frac{M_i - M_f}{M_i} 100 \tag{1}$$

$M_i$ - initial concentration of solid (t=0)
$M_f$ -concentration of solid after 3, 5, 10 and 15 min.

The stability data obtained using Andreasen pipette were compared to the sedimentation results from TURBISCAN LAb. The TURBISCAN Lab instrument belongs to the processing instruments, which has ability to backscattering light flux measurements. The TURBISCAN gives transmission and backscattering profiles over the length of the sample. The TURBISCAN Lab enables the computation of sediment profiles. Mineral suspension samples were prepared and fill the cells (around 20 ml). Automatic measurement procedure was carrying out.

## 3. RESULTS AND DISCUSSION

The production of the biosurfactants was associated with the cell growth. For biomodification purposes, the mineral particles were inoculated with the bacterium. The growth curves were obtained for *Peudomonas aeruginosa* with out or the presence of various minerals. The relationships between the cell quantity and time are presented in Figure 1 for four minerals.

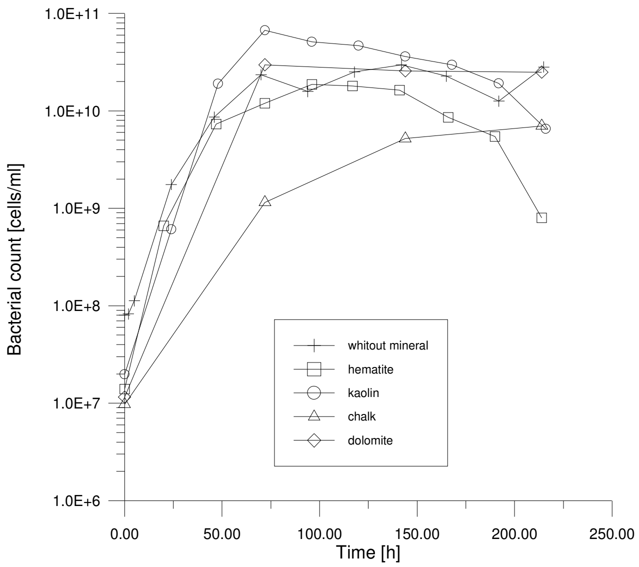


Fig. 1. Growth curves of *Pseudomonas aeruginosa* with and without of mineral particles.

The surface tension changes of supernatants during the microbial growth for various minerals are shown in Figure 2.

Mineral particles may attain an electrical charge, depending upon the pH of aqueous suspensions and the concentration of ions. In the presence of biosurfactant molecules some changes in the electrical double layer should be expected. Figure 3 presents the zeta potential data, which were collected during the growth of microorganism cells for the investigated minerals.

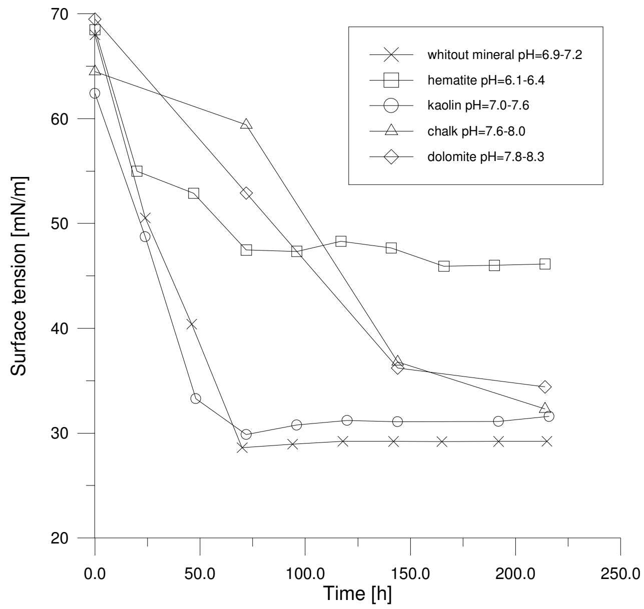


Fig. 2. The surface tension changes of supernatants during the microbial growth.

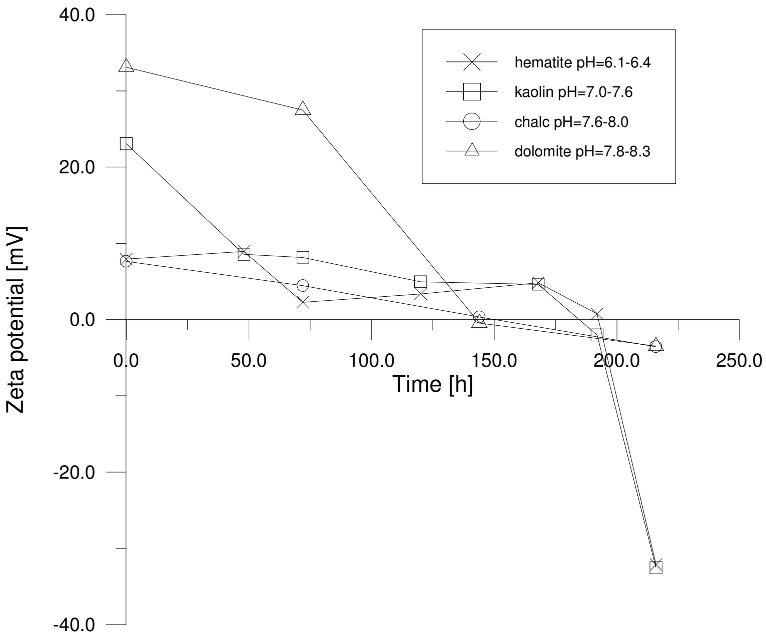


Fig. 3. Zeta potentials of mineral particles as a function of microbial growth time.

As it can be seen, the mineral particles started with positive potential. Then, the positive potential steadily decreased. The zeta potential reversal was observed on the 9th day.

Zeta potential provides an effective measurement of the potential at the solid-solution interface. The zeta potential of mineral particles was measured to determine the effect of the biosurfactant on the mineral surface charge density. The isoelectric point (iep) of the mineral is determined as the condition under, which the zeta potential is equal zero. The isoelectric point is an important characteristic of a solid-liquid interface.

Tab. 1. Isoelectric points of minerals

| Mineral | pH of isoelectric point | |
|---|---|---|
| | with bacteria | without bacteria |
| Hematite | 4.5 | 8.3 |
| Kaolin | 5.2 | 7.0 |
| Chalk | 8.0 | 8.5 |
| Dolomite | 9.5 | 12.5 |

The effect of biosurfactant addition on the zeta potential of the minerals was different among the examined minerals. After an interaction with the supernatant, the iep of the minerals was shifted to a lower pH value. For hematite the iep was shifted to pH 4.5 after interaction with biosurfactant. A small shift of iep was observed for the chalk particles. Similar behaviour of minerals has been observed by Deo and Natarajan [7].

To observe the variation in adsorbed amounts with the biosurfactant concentration, the adsorption experiments were carried out. The results shown in Figure 4 reveal that the adsorption (the surface tension different, $\Delta\gamma = \gamma_i - \gamma_{eq}$) with increasing the biosurfactant concentration ($\gamma_{aq} - \gamma_{eq}$). The sequence of adsorbed amount in all four minerals is given below:

Kaolin > Hematite > Chalk > Dolomite.

The effect of the biosurfactant addition on the stability of fines is shown in Figure 5. Generally, a number of coagulation mechanisms including charge neutralisation, bridging and hydrophobic interactions can be used to the explanation. These results suggest that bio-surfactants can be utilised as an effective reagent to stabilise as well as to destabilise of mineral suspension.

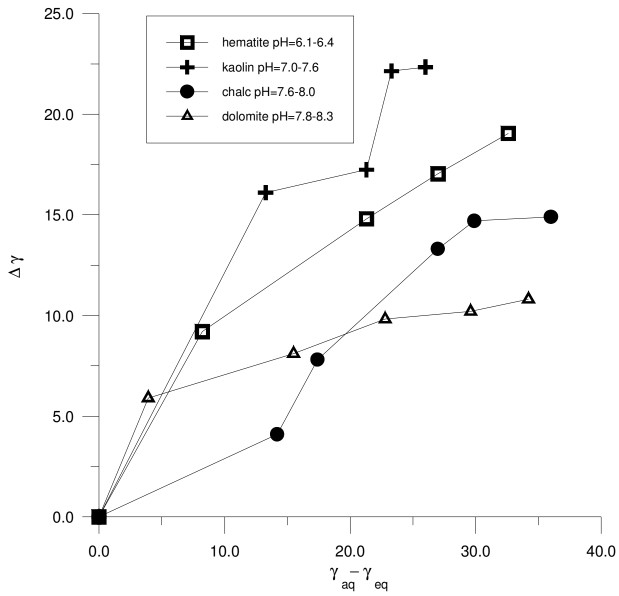


Fig. 4 The adsorption isotherm of biosurfactant on the four mineral samples

It can be seen that lower amount of biosurfactant are needed to reach the fast rate of destabilisation of chalk, kaolin and dolomite suspensions. At the higher dosage of biosurfactant (10 % v/v), the mineral suspensions are become more stabile. It is observed that high stabilisation occurs for both hematite and kaolin suspensions.

Figure 6 shows the kinetic of sediment creation as a function of the broth concentration (biosurfactant concentration). There is a good correlation between the pipette data and the scan results for both chalk and kaolin suspension. For the chalk suspension a dramatic increase of sediment thickness with increasing broth concentration can be observed. It was connected with a strong flocculation of chalk particles by biosurfactants and biopolymers.

Kaolin suspension shows a strong flocculation with 2 % v/v of broth in the solution. At the broth concentration equals 10 % v/v, a slow increase of sediment thickness was observed. The behaviour of dolomite suspension was lake kaolin suspension, however, the stability was existed at 50 % v/v of broth addition.

The interaction energy between two identical particles depends on the zeta potential and retarded Hamaker constant. Zeta potential value of about (plus or minus) 40 mV assures an energy barrier that prevents fast coagulation [8]. As seen from Figure 4 the adsorption of biosurfactant onto hematite and kaolin was bigger than the adsorption onto chalk and dolomite. The results of zeta potential measurements with minerals in broth solutions clearly indicated the value about -40 mV for both hematite and kaolin particles (Fig. 3).

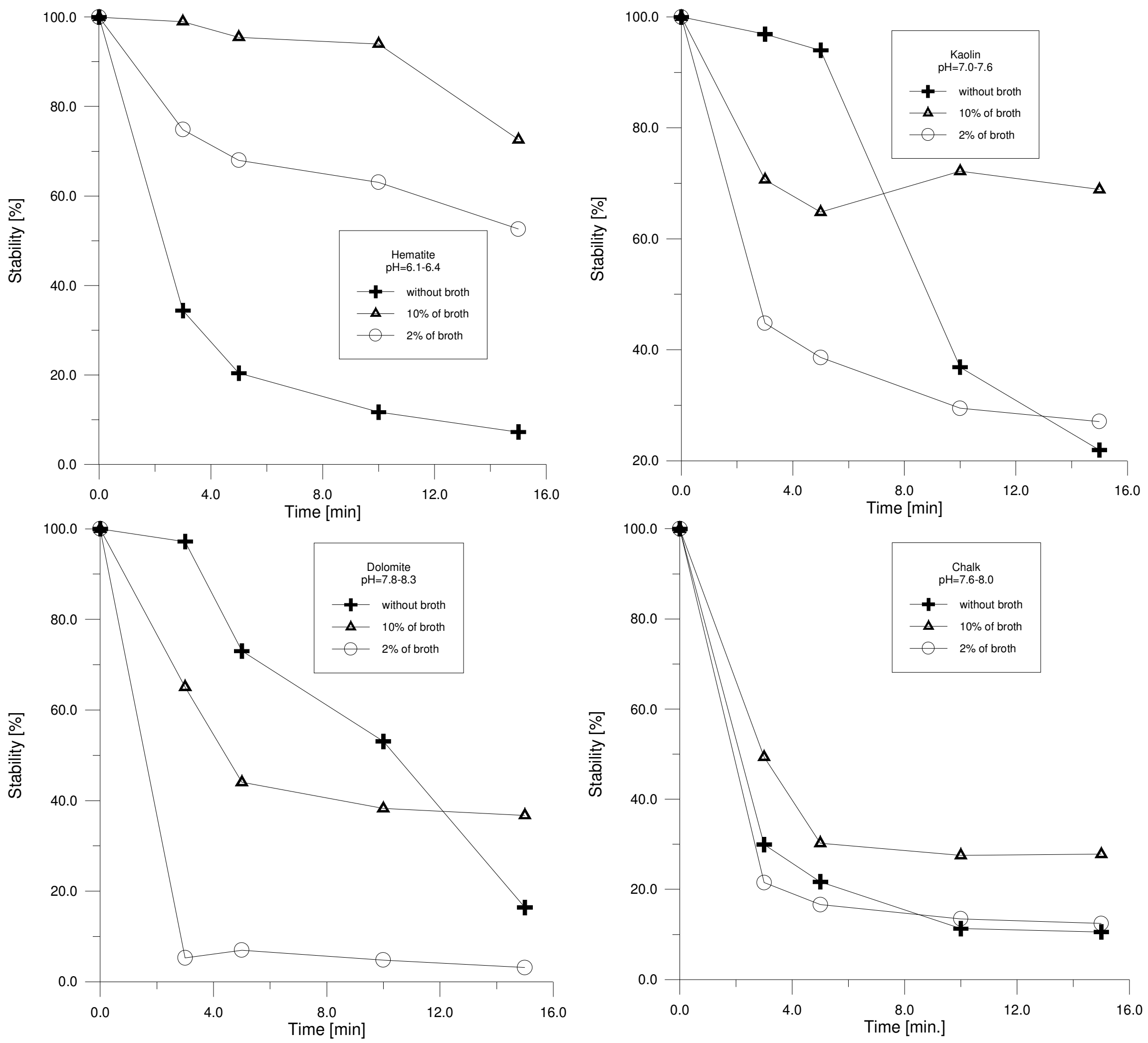


Fig. 5. Stability of mineral suspension at the presence of biosurfactant.

When discussing the stability of the suspensions, two aspects are of interest for us. One is the actual rate of the sedimentation, and other is the volume of the solid sediment solid particles. Suspensions of solid particles that have strong interparticle repulsion will sediment more slowly. When the particles have a weak repulsion or attraction they will form aggregates (flocks). The TURBISCAN measurements give a change in the sediment thickness as a function of both time and biosurfactant and biopolymer concentration.

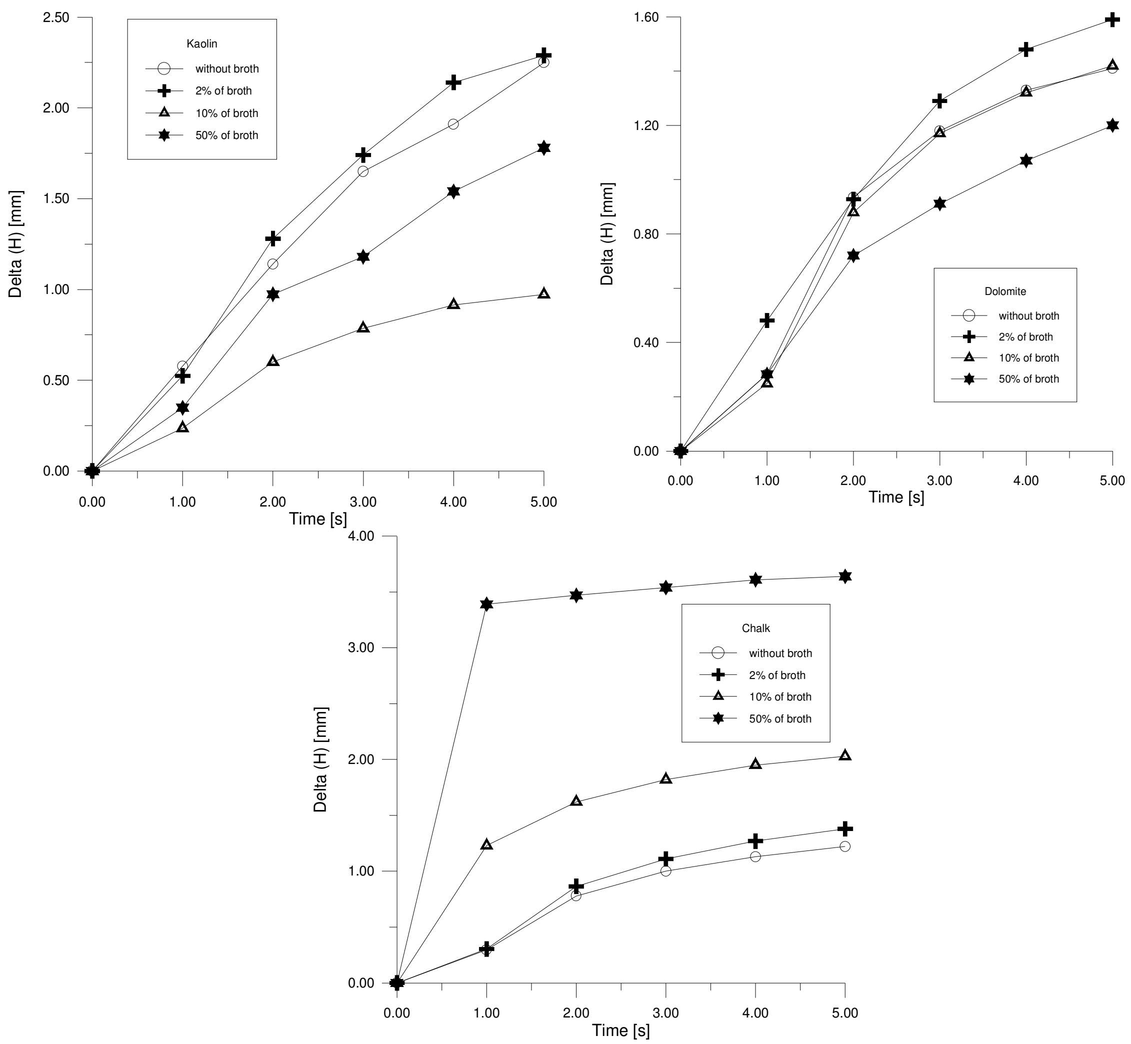


Fig. 6. Kinetic of sediment creation.

## 4. CONCLUSIONS

In this study, the attention was focused on the stability of mineral particles suspended in the various biosurfactants concentration solutions. Generally we can introduce electrostatic, steric and hydrophobic interactions for the mineral suspension behaviour explain. There are two primary conclusions that can be drawn from this work. Substantial changes occurred in the zeta potential of mineral particles after their long contact with the culture broth. Observations of the mineral suspension stability after the biopretreatment demonstrate that biosurfactants are able to stabilize of hematite and kaolin suspensions more or less effectively. It is also seen that a small quantity of broth (2%v/v) caused faster sedimentation. The several of mineral surface properties can explain the difference in the observed sedimentation of mineral suspensions.

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## CURRICULA VITAE

**Zygmunt Sadowski** was born in Wrocław at 1947. At 1970 he graduated from the Math-Phys-Chem Faculty of the University of Wrocław in Wrocław. The post-graduate study at Mining and Metallurgy University, Cracow he has got in 1973-1975. In 1978 he received his Ph.D. degree in the Institute of Inorganic Chemistry and Metallurgy at Wrocław University of Technology. In 1996, he obtained the D.Sc. degree in Maria Curie-Skłodowska University in Lublin. Since 1976 he has been employed at the Technical University of Wrocław, first at the Institute of Inorganic Chemistry and Metallurgy and since 1998 at the Institute of Chemical Engineering.

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