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SOME PROSPECTS FOR CHEMICALS RECOVERY FROM LARGE
DESALINATION PLANT BRINE EFFLUENT

P. D. Neumann

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Nuclear Desalination Program

SEPTEMBER 1967

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SOME PROSPECTS FOR CHEMICALS RECOVERY FROM LARGE
DESALINATION PLANT BRINE EFFLUENT

P. D. Neumann

ABSTRACT

The production of fresh water from the oceans will result in the production of large quantities of concentrated brines. These salt solutions contain nearly every known chemical element. The recovery of minerals from these brines has been widely suggested as a means of reducing the cost of producing fresh water. The first large-scale water desalination plant in the U.S. is planned for construction in Southern California and is to be operated by the Metropolitan Water District of Southern California.

This report summarizes a study of the potential savings in by-product recovery costs which would result from the changes in chemical and physical properties of the brine effluent from such a plant when compared to raw seawater using the MWD plant as a reference. These differences include concentrations, temperature, pH, and alkalinity.

The only recovery processes considered are those which are currently used for large-scale recovery of primary chemicals from seawater or natural brines. After a review of related recent literature, the three products judged most likely to be profitable were bromine, magnesium metal, and refined sodium chloride. Capital cost estimates and manufacturing costs estimates were assembled for plants operating on both seawater and the 2:1 concentrated seawater expected as effluent from the water plant. The savings in production costs are tabulated for each product.

An analysis of the effect of land cost on plant economics is given because of the high cost of real estate in the vicinity of the proposed MWD plant. Within the limits set for this study, only the bromine plant appears to be economically attractive.

INTRODUCTION

Recent events have virtually assured the construction of a large-scale nuclear desalination complex in Southern California. The adoption of a particular process for the Metropolitan Water District dual-purpose nuclear power desalination plant and the detailed engineering and economic analysis conducted by the Bechtel Corporation for this plant provide a firm starting point for an analysis of the potential value of by-product recovery from

the waste-brine effluent from this plant. The Bechtel Corporation analysis predicts a water cost of 27¢ per 1000 gal delivered to the Robert B. Diemer Filtration Plant, 22 pipeline miles from the plant. Industrial blocks of power in the area near the desalination plant will be available at 4 mills/kwhr.

Using the values for concentration, temperature, and flow calculated for the brine effluent from the MWD plant, four chemical plants were evaluated to determine what, if any, savings could be realized by using the concentrated brine instead of raw seawater. Plant sizes were based on reported annual rates of increased sales of magnesium metal, bromine, and refined salt. Consideration was also given to published information on minimum desirable plant sizes. Only the size of the bromine plant was influenced by this consideration.

The savings shown for chemical production are the result of using the MWD plant hot brine effluent as input to the chemical plant as compared to raw seawater. When full production is achieved at the MWD plant, 150×10^6 gal per day of waste brine at a 2:1 concentration and 80°F will be available for by-product recovery. Carbonates, bicarbonates, and carbon dioxide will have been removed by the addition of 120 ppm of sulfuric acid to the raw seawater followed by degassification.

No credit was given for reduced chemical plant area resulting from the use of concentrated brine because for most heavy industrial areas the cost of 2 to 5 acres of land is small compared to the annual savings in production costs. It should be noted that the above statement is not true for shore sites near the MWD plant or even for an island such as proposed for the MWD plant. The total cost for the 43-acre Bolsa Island and its 3000-ft causeway is estimated at \$24.1 million. The incremental land cost will be approximately \$100,000 per acre for additional acreage on the island.

At Pelican Point, 16 miles south of the proposed island, a 308-acre industrial site is valued at \$21.9 million. Grading and preparation of approximately 50 acres of the land plus a suitable access road was estimated at \$1.5 million for the desalination plant which requires sea level frontage. At this location the land and preparation costs again amount to approximately \$100,000 per acre for a chemical plant, which is not an attractive price for an industrial site. It should be kept in mind, therefore, that the

savings in manufacturing cost which are predicted apply to the process conditions and not to a particular location.

Cost estimates for equipment were obtained from several references cited in this report as well as from cost estimating literature, adjusted for capacities by a 0.6 scaling factor and to 1966 prices by an appropriate factor.

Other costs used were:

Electric power	4 mills/kwhr
Heat*	\$0.25/MBtu
Purchased H ₂ SO ₄	\$24/ton
Chlorine	\$66/ton
Sulfur	\$30/ton
Lime	\$14/ton

BROMINE PLANT

Summary

The process for extracting bromine from seawater and brines has been thoroughly reviewed in recent literature.^{1,2,3} Large commercial operations exist in the United States, Germany, Italy, Israel, and Russia. Holmes stated¹ that the minimum size plant of interest to industry is 50×10^6 lb of bromine per year. Although the rate of increase in the demand for bromine has been irregular, the average annual rate of increase from 1940 to 1965 was 7.6×10^6 lb/yr. Continued research and expansion of the non-fuel use of bromine and its compounds is expected to more than offset the reduced demand for ethylene dibromide as an additive to leaded gasoline. Most of this reduced demand results from the change-over to jet engines by military and commercial aircraft. Increasing demands for bromine are expected to come from pharmaceuticals, textiles, and photographic chemicals, as well as agriculture and the mineral separation industries.

A facility producing 50×10^6 lb/yr of bromine with an expected 90 to 95% yield would require the entire annual output of the 150 mgd desalting plant. The processes currently used for the extraction of bromine from seawater all require acidification prior to oxidation of the bromides to

*Saturated steam at 350 F.

bromine and stripping by air or other gases. Because the head-end equipment for handling large volumes of seawater could be reduced in size for a plant using waste brine from a desalting plant, substantial savings in capital costs could be realized. This would result in a significant reduction in manufacturing cost since 48% of these costs result from fixed charges. Further savings would result from the reduced requirement for stripping air due to the reduced volume of water and the increased temperature of the brine above that of seawater.

Estimated Capital Costs

Information on capital costs of bromine-from-seawater plants is very limited. The estimated capital costs shown in Table 1 are derived from figures published for the 30×10^6 lb/yr Dow plant at Freeport, Texas, and a 40×10^6 lb/yr plant in England.

Capital cost savings of 30% over a seawater plant as reported by J. M. Holmes¹ were used to estimate the capital costs. These savings result from a 50% decrease in the size of blowing-out towers, seawater pumps, and fans for blowing air.

Estimated Operating Costs

A bromine plant operating on desalting plant waste brine having a concentration ratio of 2:1 and an 80°F temperature would have significant operating advantages over a plant producing the same tonnage of bromine from seawater. The savings in power costs for pumping water into the 50×10^6 lb/yr plant based on identical supply lines (3000-ft intake line, 30-ft rise) amounts to approximately \$139 per stream day when a 4 mills/kwhr power cost is assumed. Even greater power savings result from the reduced requirement for blowing air. A 50% reduction was assumed as a result of the 2:1 concentration ratio and an additional 30% reduction in the air requirements was estimated from data published for seawater over the range of 65 to 80°F.

It is anticipated that no additional sulfuric acid will be required by the bromine plant after startup. The brine effluent from the salt water plant will have been treated with 120 ppm sulfuric acid based on

Table 1. Savings in Production Cost - Bromine

Capital investment for plant operating on seawater: \$17,750,000
 Capital investment for plant operating on MWD brine: \$11,765,000
 Production: 50×10^6 lb/yr from 150×10^6 gal/day of MWD brine

	Savings in Dollars Per Stream Day
1. Electricity	\$ 495
2. Sulfuric acid	--
3. Sulfur dioxide	--
4. Chlorine	--
5. Labor	--
6. Maintenance materials	90
7. Maintenance labor	87
8. Payroll extras	14
9. Overhead	30
10. Fixed charges	3808
	<hr/>
Total savings	\$4524
3.0¢/lb of product	
Current market price 21¢/lb	

raw seawater. Sulfuric acid is formed in the bromine recovery process by the oxidation of SO_2 by bromine to form sulfuric acid and hydrobromic acid. Subsequently, the hydrobromic acid is reacted with chlorine to recover bromine. The hydrochloric acid which is produced is recycled along with the sulfuric acid to acidify the incoming feedwater in plants operating on raw seawater (see Fig. 1). Under normal conditions this supplies over half of the 140 ppm acid requirements of a bromine-from-seawater plant. A 50×10^6 lb/yr bromine plant coupled to a 150 mgd desalting plant would produce the equivalent of 75 tons/day of excess sulfuric acid, which is roughly half the requirements of the desalting plant (see Fig. 1). This acid would have a value of over \$500,000 per year to the desalting plant based on the \$24/ton price used in the MWD cost analysis. An additional capital investment of about \$100,000 would permit recycling this acid to the desalting plant. If the bromine plant pays to the desalting plant the market price of the additional acid required by the two-plant complex and returns waste acid from the bromine process at no cost to the water plant, the net savings to the water plant amounts to about 2.6¢ per 1000 gal of water produced. The bromine plant, taking advantage only of the increased temperature and concentration of the seawater, pays as much for its total acid requirements as a bromine-from-seawater plant and still realizes a savings of 3.0¢/lb of product. This gives a minimum credit for the by-product acid; other conceivable acid exchange agreements between the bromine and water producers could increase the total benefit to the bromine producers by 3 to 5%.

The estimated savings in manufacturing costs tabulated in Table 1 are based on a fixed charge rate of 21% yearly¹ and maintenance labor cost and materials cost each at 0.0015% of capital investment per stream day.⁴ No credit is assigned to the bromine plant for reduced manufacturing labor cost which might result from the reduced size of the head-end process equipment. A reduction in manufacturing costs of about 3¢/lb of bromine is calculated for a plant of this size operating on a 2:1 concentration of seawater at an inlet temperature of 80°F and free of carbonate and bicarbonate alkalinity.

(a)

ACID BALANCE FOR BROMINE-FROM-SEA-WATER PLANT

* EQUIVALENT TO 185,917 lb H₂SO₄
AND TOTAL ACID CONSUMPTION OF
424,959 lb H₂SO₄

(b)

ACID BALANCE FOR BROMINE-FROM-DESALINATION-PLANT-WASTE

* EQUIVALENT TO 110,272 lb H₂SO₄
AND TOTAL ACID CONSUMPTION OF
424,958 lb H₂SO₄

Fig. 1. Acid Balance for Bromine Production.

MAGNESIUM PLANT

Summary

The world-wide demand for magnesium and its alloys and for several forms of magnesium compounds has risen steadily over the past 10 years. The encouraging future for magnesium production was recently confirmed by announcements that Dow Chemical Company^{5,6} will increase its production for the third time in as many years. It will increase production by 50×10^6 lb/yr by modernizing and starting up the remaining half of its plant capacity at Freeport, Texas, which has been idle since 1957. Likewise, Alamet Corporation at Selma, Alabama, announced⁶ that it would increase production by 25% by installing additional processing facilities. With this expansion currently in progress and increasing consumption forecast for several years, it seems reasonable that another plant equal in size to the Dow plant will be required in the next few years. The U. S. Bureau of Mines⁷ predicts an annual domestic demand of 85,000 tons in 1970 increasing to 170,000 tons in 1980. The production of 36,000 tons per year of magnesium metal would consume only 11×10^6 gal/day of the water plant waste brine.

World-wide demands for other magnesium compounds, such as magnesium oxide and oxychloride, are certain to grow for many years. The U. S. production of magnesium oxide from seawater, brines and seawater bitterns increased from 200,000 tons in 1954 to 630,000 tons in 1963. No mixed-product plants were considered in this analysis because of the infinite number of product ratios to choose from.

The savings which can be achieved in the production of magnesium by using a desalting plant waste brine as compared to raw seawater are extremely small. Significant savings in capital investment are confined to the inlet water pumping and first-stage precipitation only.

All other equipment would be identical. Some small savings in chemical costs might result in the neutralizing step because the brine effluent from the desalting plant is essentially free of carbonate and bicarbonate ions and CO_2 . As a result, very little or no calcium carbonate would precipitate when the lime-caustic reagent is introduced to bring down magnesium

hydroxide in the first stage of magnesium recovery. The resulting filter-cake of magnesium hydroxide could then be converted to the chloride with very little excess hydrochloric acid and might be pure enough to go directly to the evaporator without the addition of magnesium sulfate to remove calcium. The savings in capital and operating costs resulting from this minor change would be small compared to the totals.

Estimated Capital Costs

Capital costs of a plant the size of the Dow Chemical Company plant in Velasco, Texas, are reported to be very near \$1,000 per annual ton of product.⁸ Savings in equipment cost for a 50% reduction in volume of the incoming water are estimated to be \$568,000 based on costs obtained from Dorr-Oliver, Inc. This represents approximately \$1,443,000 savings in capital investment when the usual factor of 2.54 is used to derive total cost from equipment cost.

Estimated Manufacturing Cost

In this process no significant savings result from the use of the reference brine as compared to seawater. The reduction in pumping cost, maintenance, and overhead are of little importance in total cost of production. The reduction in fixed charges resulting from the capital savings quoted above amount to approximately 1% of the 1966 sale price of 35¢ per lb.

Using the published cost data^{1,7,8} and applying the same factors as for the bromine plant, a total cost of 26.6¢/lb was calculated. If the in-plant cost of electric power in the Texas plant is only 3.4 mills as reported,⁸ the increase in the cost of electricity from 3.4 to 4.0 mills will result in an increase in production cost of 4.8 mills/lb which completely offsets the 4 mills/lb savings estimated in Table 2.

Greater savings are no doubt obtainable through improvements in technology and efficiency. The Velasco plant was reported¹⁷ to have operated at 121% of its rated capacity with a manufacturing cost of \$0.1151/lb of magnesium metal. These improvements would also be incorporated into a new plant. However, some incentive other than the 2:1 increase in concentration would be necessary in order to influence a decision to

Table 2. Savings in Production Costs - Magnesium Metal

Capital cost of plant operating on seawater: \$72,000,000
 Capital cost of plant operating on MWD brine: \$70,557,000
 11×10^6 gal/day of MWD brine to produce 36,000 tons/yr of product

Item	Savings in Dollars Per Stream Day
1. Raw materials	--
2. Electricity (pumping)	\$ 10
3. Labor	--
4. Electrodes	--
5. Maintenance materials	21
6. Maintenance labor	21
7. Payroll extras	3
8. Overhead	7
9. Fixed charges	918
Total savings	\$980
\$0.004/lb of product	
Current market price 35¢/lb	

expand production through a new plant near a desalination plant rather than by expansion of existing plants. A combination of a large local market along with very cheap land and at least equal labor and power costs might provide the incentive. These criteria certainly could not be met in the vicinity of the MWD plant.

REFINED SALT

Summary

It became evident early in the analysis that a flash crystallization plant operating on MWD effluent could not compete with the production of crude salt and brines from other available sources. Therefore, only the production of refined salt is considered here. Production and consumption of refined grades of sodium chloride in the U. S. have been remarkably constant for several years. Shipments whose destination was the southwestern states, however, increased by nearly 100,000 tons from 1963 to 1964 and have steadily increased since. It is expected, therefore, that the output of a plant with an annual production of 200,000 tons could be readily consumed in that area. For the purpose of this study one solar evaporator plant and one flash crystallization plant were investigated to compare production costs with current sales prices for refined salt only.

Significant savings were found for both the solar evaporation and flash crystallization process when compared to plants operating on raw seawater. However, the solar evaporation plant was the only one which showed actual production costs less than the value of products. This fact probably accounts for the absence of any known references to flash crystallization plants operating on raw seawater.¹⁰

Flash Crystallization

To produce 200,000 tons per year (650 tons per day) of salt from the reference brine would require a daily input to the flash plant of 3.35×10^6 g. Of this, three million gallons could be recovered as distilled water. Credit was given to the process for this water at the rate of 20¢ per 1000 gal delivered to the product water sump at the nuclear desalting plant.

The process used as a model to obtain these data is one proposed by Messing¹¹ in 1965 and is based on current technology. In this plant, as in the other studied, fixed charges are the largest single item in production costs. They amount to approximately 53% of the total.

Energy cost is the second largest item for this process and at the rate of \$0.25* per million Btu accounts for 21% of the cost of production. For this reason, significant savings in manufacturing cost result from a 50% reduction in the size of the evaporators and the accompanying 50% reduction in heat load. Table 3 summarizes the reduction in manufacturing expenses. As noted, however, these savings are relative. The actual cost of producing salt by this process would exceed its market value by approximately \$1.25/ton because of the large capital expenditure required and the cost of heat to evaporate water. An increase in the concentration of salt in the brine to a ratio of 4:1 (compared to seawater) makes this process a profitable one.¹¹

Refined Salt by Solar Evaporation

The production of sodium chloride by solar evaporation of seawater has been practiced for at least four thousand years.^{2,3,9} In 1964, solar salt accounted for 5.8% of the total of 31.6 million tons of salt of all grades produced in the U. S. and 37% of the 4.7 million tons of refined salt. In locations such as California's Pacific Coast where solar evaporation of seawater is profitable, the solar evaporation of desalting plant waste brines would enjoy a significant savings in production costs. This reduction in cost results from the reduced acreage of evaporation ponds required to produce a given amount of salt.

Capital Savings

A plant to produce 200,000 tons per year of salt from the reference brine would require the evaporation of 10.1 acre-ft per day of water. Using an average evaporation rate for the southwestern states of 40 inches per year sets the surface requirements for evaporation ponds at approximately 1000 acres.^{12,13,14} Twice that area would be required to produce the same tonnage from seawater. A few additional acres would be required for crystallizing ponds. In most locations the ponds must be lined¹² to prevent

*Saturated steam at 350°F.

Table 3. Savings in Manufacturing Cost for
Flash Crystallization - Salt Plant

Capital cost^a of plant operating on seawater: \$12,128,000
 Capital cost^a of plant operating on MWD brine: \$8,524,000
 3.35 x 10⁶ gal/day of MWD waste brine to produce 650 tons/day
 of refined salt

Item	Savings in Dollars Per Stream Day
1. Heat (1.2 x 10 ¹⁰ Btu at \$0.25/10 ⁶ Btu)	\$3,000
2. Electricity (7,500 kwhr at 4 mills)	30
3. Labor (3-man shift)	274
4. Maintenance labor	57
5. Maintenance material	54
6. Payroll extras	47
7. Overhead	110
8. Fixed charges	2,294
9. Credit for sale of water	600
Total savings	\$6,166

\$9.48/ton of product

Current market price \$17/ton

^aEquipment list and prices in ref. 8 scaled up and converted to 1966 prices.

excessive leakage. This lining represents the major capital cost. Where soil conditions permit the construction of unlined solar ponds, production costs are greatly reduced.^{7,14} For the purpose of this analysis, it was assumed that linings would be required.

Several types of films have been evaluated in studies sponsored by the Office of Saline Water.^{15,16} Concrete and soil-cement linings have also been used.¹² Because of the nature of the harvesting operation and the use of heavy machinery, the soil-cement lining was chosen as a basis for economic evaluation. Table 4 lists the estimated costs of the various types of linings evaluated.

Table 4

Lining	Installed Cost Per Acre
10-mil black polyethylene	\$ 9,580
Soil-cement	5,500
Concrete	8,900
1/32-in. butyl rubber	15,200

It should be noted that this type of plant differs greatly from the conventional chemical plant in that no instrumentation, very few service facilities and buildings, and no chemical processing equipment with its associated pumps, wiring, piping, and instrumentation is required to produce a product containing 99.4% NaCl. Drying kilns and crystallizers for purification to 99.9% would account for only 7 to 10% of the capital cost of the plant.

The standard 10% figure was used to estimate contingency and engineering costs, although it is unlikely that these costs would run that high for such a simple construction project.

The reduction in the cost of solar ponds using the figure for soil-cement lining would amount to \$5,500,000. In addition, the cost of pumps and piping for brine supply would be reduced by approximately \$15,000.

These result in a total savings in capital and related costs of \$6,273,000. The fact that over 1100 acres of flat land is required to support an operation of this size makes it apparent that the cost of land would be a major influence in the location of such a plant.

Savings in Manufacturing Costs

Other differences between this type of plant and the more conventional chemical plant can be seen in the maintenance costs and cost of storage facilities. The average maintenance costs for liquid-solid chemical process plants runs about 0.0015% of plant investment per day. For a solar plant this figure increases to about 0.0024%.¹² The storage facility must be capable of storing a large percentage of the annual production due to the seasonal character of production in most locations and the possibility of slow-down due to periods of adverse weather. The potential savings, however, make this a very attractive process. As summarized in Table 5, the estimated savings in production costs amount to nearly \$7/ton of product. With the 1966 price of refined salt averaging near \$17/ton, this represents a very attractive savings in production costs.

Salt is a cheap, bulky commodity, and transportation charges are an important part of the total cost to the consumer. For this reason, most salt is sold near the point of production. Salt is sold on a delivered basis and for this reason the production is a highly competitive industry, depending on high sales volume and low unit costs.

REAL ESTATE COSTS

The effect of real estate prices on the operating cost of the processes being reviewed here is of interest. Although the fixed charges assigned to real estate investment vary greatly, for the purpose of this analysis the 21% fixed charge rate was used. On this basis, an investment of one million dollars results in a daily cost of \$636, or, conversely, each \$1.00 savings in daily operating costs allows an additional capital investment of \$1,571.

Table 5. Savings in Production Costs - Solar Salt

Capital cost for plant operating on seawater: \$13,436,000
 Capital cost for plant operating on MWD brine: \$7,163,000
 1.1×10^9 gal/yr of MWD brine to produce 200,000 tons of refined salt

Item	Savings in Dollars per Day
1. Electricity	\$ 4
2. Maintenance at \$0.193/acre/day	174
3. Labor	--
4. Payroll extras (15% of labor cost)	13
5. Overhead	30
6. Fixed charges	3992
Total savings	<u>\$4215</u>
\$6.95/ton of product	
Current market price \$17/ton	

In the case of the bromine plant, the estimated daily savings in production cost over those of a plant operating on raw seawater means that this plant can invest a total of \$7.9 million in land or other capital items and still extract bromine at the same cost as the bromine-from-seawater plant. Thus, if 50 acres is required for the site, the maximum price that can be paid for land is \$158,000 per acre, or, if land can be purchased for \$100,000, as seems likely, a 79-acre site can be purchased. It seems likely that a bromine plant would be economically attractive even in Southern California.

As stated previously, the cost of recovering salt from a brine of only 2:1 concentration by flash crystallization would be prohibitively high even if land were free. In the case of a magnesium plant requiring 50 acres and the solar salt plant requiring 1,000 acres or more, the maximum allowable price for land would be \$30,000 and \$6,600 respectively.

CONCLUSIONS

For the bromine and salt plants, fixed charges amounted to 50% or more of the total cost of manufacture. It is obvious, therefore, that reducing capital costs holds the greatest promise of savings. In bromine and salt extraction plants, capital costs are directly proportional to the volume of water pumped into the plant to produce a given weight of product. These plants could benefit from further increases in the concentration ratio of the brine.

Such is not the case for magnesium plants. The major part of the capital investment is in the electrolytic cells and chemical process equipment which depends only on the product output of the plant. The head-end process equipment consisting of lime slakers, mixing and settling tanks is relatively inexpensive. Its contribution to capital cost is small. On the other hand, process improvements which allow a production rate of 121% of rated capacity have the effect of reducing capital cost per annual ton by 16% - a substantial reduction. It seems likely that new demands will be met by expansion of existing plants in Texas, California, Alabama, and possibly Nevada rather than by new plants.

The necessity of keeping capital investment to a minimum reduces the likelihood that any of these by-product recovery plants would be able to locate near the MWD desalination plant because of the high cost of land. This is particularly true of the solar salt which would require over 1000 acres of land. The smallest plant in physical size would be the flash crystallization plant for salt recovery. A minimum of 10 acres is probably required for such a plant. At the prices quoted for industrial real estate in the vicinity of the proposed MWD water and power plant, the investment in land and site preparation would amount to \$1,000,000. The bromine and magnesium plants require 40 to 50 acres each, and the solar-salt plant requires about 1000 to 1100 acres.

As long as the desalination plant is unable to extract more than half the water from seawater, the flash crystallization salt plant is unlikely to be profitable regardless of the cost of land. The bromine plant may have a sufficient advantage over seawater plants to be able to compete with them at the land prices quoted above even if the desalting plant is given the benefit of 2.6¢/1000 gal savings in acid cost.

Locating a magnesium plant near the desalination plant cannot be justified on the basis of using concentrated seawater from the water plant. It must depend on other incentives, such as local markets and reduced transportation charges. The solar-salt plant can profitably locate only where land prices are much lower.

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