The Use of Bromine Chemistry for Sand Filter Disinfection

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An integrated, heavy industrial manufacturing facility involved in the casting of metal alloys, machining, and electroplating of large engine components was having difficulty maintaining flow through their wastewater sand filter. The filter is used to remove suspended solids from the wastewater clarifier effluent prior to discharge to the municipal sewer system. Sodium hypochlorite was applied continuously to the clarifier effluent for disinfection, but frequent sand filter malfunctions still occurred as a result of biomass accumulation on the sand media, coupled with the deposition of inorganic salts. By implementing a treatment program utilizing bromine chemistry for sand filter disinfection, the plant was able to eliminate bioaccumulation and inorganic salt deposition on filter media. As a result, sand filter maintenance downtime was reduced 50 %, and chemical costs were reduced 40 %. Overall, sand filter maintenance costs were reduced and wastewater compliance enhanced via increased sand filter efficiency.

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Introduction

An integrated, heavy industrial manufacturing facility involved in the casting of metal alloys, machining, and electroplating of large engine components was having difficulty maintaining flow through its wastewater sand filter. The filter is used to remove suspended solids from the wastewater clarifier effluent prior to discharge to the municipal sewer system. Initially, hydrogen peroxide (35% active) was continuously fed to the clarifier effluent to prevent biofouling on the filter media. Frequent accumulation of biomass on the filter media resulted in excessive filter downtime.

In an effort to resolve the biofouling problem, the plant incorporated a biocide program utilizing the continuous application of sodium hypoclorite (15% NaOCl). This program satisfactorily controlled microbiological growth, but the large amount of NaOCl required caused treatment chemical cost to be high. In addition, the application of NaOCl (pH of 12.5) to alkaline clarifier effluent (pH of 9), increased the scaling tendency of the water. Deposition of calcium carbonate and calcium sulfate on the filter media caused the filter to malfunction after only 6 months of service on this program. The media had to be acid cleaned to remove the accumulated calcium scale.

A chemical treatment program was required that would effectively and economically control filter biofouling, and yet reduce the tendency for scale buildup on the filter media. Knowing that the effectiveness of chlorine was dependent on pH, the water treatment representatives recommended that a bromine-based biocide be considered as a replacement. A study was undertaken to evaluate the biocidal efficacy of bromine versus chlorine using the plant's current wastewater chemistry parameters.

Biocidal Efficacy of Bromine versus Chlorine

Chlorine and bromine based biocides are oxidizing biocides. Oxidizing biocides oxidize or accept electrons from the cellular material or critical enzymes within the bacterial cell, which leads to cell death. In water, sodium hypochlorite ionizes to hypochlorous acid (HOCl) and hypochlorite ion (OCl^-).

$$NaOCl \leftrightarrow Na^+ + 2OCl^-$$

$$2OCl^- + H_2O \leftrightarrow HOCl + OCl^- + OH^-$$

The most cost effective bromine donor available is sodium bromide (NaBr). Sodium bromide is commercially available as a 40% solution. Concentrated sodium bromide solution is completely non-toxic and is not a biocide. However, when this concentrate is mixed with sodium hypochlorite, the hypochlorite is reduced and the bromine is oxidized to hypobromous acid (HOBr) and hypobromite ion (OBr^-).

$$NaOCl + NaBr + H_2O \leftrightarrow HOBr + OBr^- + NaCl$$

The concentration of each species is primarily dependent on pH. Of the chlorine and bromine species formed, the major oxidizing power is found in the hypohalous acid form (HOCl and HOBr).

Effectiveness

The biocidal effectiveness of HOCl and HOBr are considered to be comparable by most researchers. HOBr however, was found to kill more rapidly than HOCl. The significant attributes of HOBr over HOCl are due to stability at alkaline pH, and the relative effectiveness of bromine derived species. *Table 1* lists the commonly found chlorine and bromine derived species, and compares their relative biocidal efficacy.

Table 1
Relative Oxidizing Power of Halogen Species

Halogen	*Species*	*Oxidizing Power*
Hypochlorous acid	HOCl	1.0
Hypobromous acid	HOBr	1.0
Dibromamine	$NHBr_2$	0.9
Monochloramine	NH_2Cl	0.2
Hypobromite	OBr-	0.05
Hypochlorite	OCl-	<0.05

- Sodium hypochlorite efficacy studies in the laboratory indicate that OCl- is only 1/20 to 1/300 as effective as HOCl. OBr- is slightly more effective than OCl-.

- In the presence of ammonia, chloramines and bromamines can be formed. Chloramines are only 1/5 as effective as HOCl and HOBr.

- Bromamines are considered to be almost as effective a biocide as HOBr. This may be due to the instability of the bromamine compounds, which results in their rapid deterioration to HOBr.

The bromine-derived species provide more overall oxidizing power than chlorine derived species.

Comparative HOCl and HOBr Concentration versus pH

The dissociation of hypochlorous acid and hypobromous acid in water is an equilibrium reaction controlled by pH. The relative concentration of HOCl and HOBr versus pH is illustrated in *Figure 1*. As the graph indicates, the dissociation of hypochlorous acid to hypochlorite ion proceeds rapidly as the system pH increases above 6.5. At a pH of 9.0, characteristic of that found in the plant's clarifier effluent, only 3% of HOCl formed, remains. Conversely, approximately 33% of HOBr formed, remains at a pH of 9.

Theoretical Comparison of the Amount of HOBr Generated Using NaBr/NaOCl versus the Amount of HOCl Generated Using NaOCl

This section compares the amount of HOBr generated using NaBr/NaOCl versus the amount of HOCl generated using NaOCl alone. The comparison is theoretical, using stoichiometric formulas for the generation of HOBr and HOCl. Chemical and/or biological demand is not taken into account. Plant biocide dosages and wastewater chemistry values were used to calculate HOCl concentrations present via the use of NaOCl.

Calculations

Molecular weights

Cl_2	79.9
HOCl	52.5
NaBr (40%)	257.5
NaOCl (15%)	644
HOBr	96.9

Assumptions

- NaOCl use is 40 gallons per day
- Sodium bromide solution is supplied is 40% active
- NaOCl solution is 15% active as chlorine
- System pH is 9.0
- 1 gallon of 15% bleach = 1.25 lbs. as Cl_2
- Density of 15% bleach = 10.1 lbs./gal.
- Density of NaBr (40% solution) = 11.9 lbs./gal.

Formulas

1 Mole Cl_2 ↔ 1 Mole HOCl
1Mole HOBr is equivalent to 1 Mole HOCl
1 Mole NaOCl + 1 Mole NaBr (40%) ↔ 1Mole HOBr

Calculations

1. *Total Cl2 available using 15% NaOCl*

40 gal. NaOCl X 1.25 lb. Cl_2/gal. NaOCl = *50 lb.* Cl_2

2. *Total HOCl generated by 50 lbs. of Cl2*

$$\frac{Cl_2\text{ (lb.) X mol. wt. HOCl}}{\text{Mol. wt. }Cl_2} = \text{HOCl (lb.)}$$

$$\frac{50\text{ lb. }Cl_2\text{ X }52.2}{79.9} = \textit{32.7 lb. HOCl}$$

3. *Total HOCl available at pH of 9.0 (see Fig. 1)*

32.8 lbs. HOCl X 0.03 = *1.0 lbs. HOCl*

4. *Amount of HOBr needed to equal quantity of HOCl generated at pH 9 (see Fig. 1)*

$$\frac{\text{1.0 lbs. HOBr}}{0.33} = \textit{3.0 lb. HOBr}$$

5. *Quantity of NaBr (40%) needed to generate 3.0 lbs. HOBr*

$$\frac{3.0 \text{ lb.HOBr} \times 229 \text{ (mol. wt. NaBr)}}{96.9 \text{ (mol. wt. HOBr)}} = 7.1 \text{ lb. NaBr}$$

6. *Quantity of NaOCl (15%) needed to oxidize NaBr to HOBr*

$$\frac{3.0 \text{ lbs.HOBr} \times 644 \text{ (mol. wt. NaOCl)}}{96.9 \text{ (mol. wt. HOBr)}} = 20.0 \text{ lbs.}$$

Results

- Based on the above assumptions, the daily amount of chlorine (as Cl_2) added to the system via the use of 40 gallons of NaOCl is *50 lbs.*
- Using the stoichiometric formula for HOCl generation (see calculations), *32.8 lbs. of HOCl* is formed from 50 lbs. of chlorine .
- Using the attached graph titled, "Equilibrium of Bromine and Chlorine in Water at Various pH Levels", at a pH of 9.0 there is approximately *1.0 lb. of HOCl available.*
- Using the stoichiometric formula for HOBr generation using one mole of NaBr and one mole of bleach to produce 1 mole of HOBr (see calculations) at a pH of 9.0, *3.0 lbs. of HOBr* would be required to provide 1.0 lbs. of available HOBr (equivalent to amount of HOCl available using NaOCl - see above).
- The quantity of 40% NaBr needed to generate 3.0 lbs. HOBr is 7.1 *lbs. NaBr (40% active) = 0.6 gallons of NaBr*
- The quantity of bleach required to activate 8.0 lbs. of NaBr is *20.0 lbs. bleach (approximately 2.0 gallons).*

Treatment Action Plan

Based on the theoretical comparison of HOBr versus HOCl at a pH of 9, it was evident that much less NaBr and NaOCl would be required to equal the oxidizing power of the that using NaOCl alone. Therefore a considerable cost benefit would be realized using NaBr/NaOCl rather than NaOCl alone.

An on-line trial was begun to evaluate the actual effects of sand filter disinfection using sodium bromide activated by sodium hypochlorite.

The plant wastewater treatment system was in operation for seven hours each day. Plant personnel identified that in the past, the majority of filter biofouling took place during the period the sand filter was not operating. The water treatment field representative asked the plant to add bromine biocide to the clarifier effluent twice each day:

1. During daily wastewater system start-up for ten minutes.
2. During daily wastewater system shutdown for ten minutes.

Utilizing this schedule of biocide addition, the sand filter was disinfected at the start, and ending of each operating day. This allowed concentrated biocide to kill bacteria that grew during system lay-up, and allowed concentrated biocide to remain in contact with filter media after the system was shut down for the day.

During each biocide feed injection, one half gallon of sodium bromide solution was added to one and a half gallons of 15% sodium hypochlorite solution. The sodium bromide solution was pumped directly into the sodium hypochlorite pump discharge line approximately 15 feet upstream from its discharge to the clarifier effluent. Injection of the sodium bromide at this location allows the sodium hypochlorite to completely oxidize the sodium bromide to hypobromous acid prior to its discharge into the clarifier effluent water. The on-line trial was begun in May 1999, and is ongoing at this time.

Treatment Results

The sand filter disinfection program using sodium bromide activated with sodium hypochlorite has been in-service for the past six months. The results of the biocide treatment program are as follows:

- There has been no visible evidence of biodeposition on filter media.
- No maintenance activities have been required on the filter system other than routine service. The

filter media has remained free of scale deposition

- Filter disinfection treatment chemical costs have been reduced by 60% as compared to the chemical cost of using NaOCl alone. *Table 2* illustrates the comparative chemical cost of the treatment programs utilized.

Table 2
Sand Filter Disinfection Chemical Cost

Disinfection Program	Weekly Chemical Use (gallons)	Weekly Chemical Cost
Hydrogen peroxide (35%)	75	$213.00
NaOCl (15%)	300	$240.00
NaBr (40%) NaOCl (15%)	7 21	$77.00 $17.00

Conclusions

The performance of bromine-based biocides for the disinfection of sand filters in an alkaline pH environment is superior to that of chlorine-based biocides. Sodium bromide solution activated with sodium hypochlorite generates 90% more hypohalous acid than is generated using sodium hypochlorite alone in water with pH of 9.

After an extended trial period of 6 months, the following treatment benefits were gained:

- *Sand filter disinfection chemical cost was reduced 61%.*

- *Maintenance costs were reduced more than 50% as a result of the elimination of biodeposits, and a reduction in scale deposition.*

- *On-going regulatory compliance for metals was realized as result of decreased sand filter downtime.*

References

Frank N. Kramer, *The NALCO Water Handbook*, McGraw-Hill Book Company, New York, NY, 1988; pp. 22.9-22.12.

Betz Laboratories, Inc., *Betz Handbook of Industrial Water Conditioning,* Betz Laboratories, Inc., Trevose, PA, 1991; pp.200-201.

Figure 1
Dissociation of HOBr and HOCl versus pH