

Blending HBr with Bleach to Form Hypobromous Acid (HOBr)

Hypobromous acid can be efficiently and quickly blended on site using several methods. Both of them differ in the chemical kinetics and attributes, but both methods are based on the basic equation:



Hydrogen Bromide:

Hydrogen bromide is the only known acid (mineral or organic) to react with chlorine or bleach to form a further non-hazardous product, hypobromous acid, and does not create noxious chlorine gas at concentrations less than 2%, [20,000 ppm], by wt.

The precursor is an acid, but it has no odor or fuming characteristics. It is far safer to handle than hydrochloric acid (muriatic acid). The shelf life of the product is several years if kept at normal ambient temperatures and out of the direct sunlight. Direct sunlight will have a negative impact on the appearance of the product by changing the color from clear to degrees of yellow or orange. The orange color is bromine (Br₂), which is normally not a problem, but if allowed to remain in the sunlight more bromine will develop, which will have a distinct pungent odor. The solution is still **use-able** in the "yellow-orange" state, but these conditions should be avoided by not allowing the precursor to be subjected to direct sunlight (UV) or excessive continuous heat to allow the temperature of the bulk liquid to exceed 90° F.

Mixing Methods/Discussions:

1) Basics:

Hypobromous acid is easily and quickly created by mixing hydrogen bromide and sodium hypochlorite (bleach) in water. This can be done in a pipe "in-line" or by utilizing a dilution "blending" tank. The user may wish to blend hydrogen bromide and bleach directly into a line and have it used downstream quickly. Or one may choose to blend together more concentrated solutions in a blend tank, which in turn may be the source for chemical pumps to utilize as the feed stock for multiple remote applications.

Hypobromous acid degradation rate accelerates with increasing concentrations. The decay rate for a 200–300 ppm solution of available bromine would result in a half-life of about 10 days, whereas a 4000 ppm solution may only have a half life decay rate of only a few hours or less. The loss of bromine activity is quite natural, and the solution can be "re-generated" by adding sufficient bleach to bring the pH into the 6.9–7.4 range.

When hydrogen bromide and bleach are added in the correct proportions, the pH of 6.9–7.4 will always be the result, regardless of the hardness or alkalinity of the feed water. The decay of hypobromous acid always results in either hydrogen bromide or bromine (Br₂) formation, or a mixture of both, because the decay of hypobromous acid is an acid-releasing process. At higher temperatures this decay rate increases proportionally with the rise in temperature. As the pH drops, the decay of hypobromous acid accelerates and it becomes an autocatalytic process. At concentrations less than 1,000 ppm this is a slow and relatively harmless side reaction. Keep in mind that over time the hypobromous acid is unstable and wants to revert to its original state as hydrogen bromide, which is the reason for the drop in pH.

In almost all cases, a pH meter is required to monitor the efficiency of the reaction or feed rates of the chemicals. It stands to reason if the hydrogen bromide pump stopped the pH would go up, due to the high pH of the bleach solution. And conversely, if the bleach pump stopped, the pH would go down. Both scenarios would trigger an alarm warning, alerting the user to a fault condition.

2) In-Line Blending:

This method typically involves using chemical pumps to inject hydrogen bromide and bleach into a water line, in the same order. Hydrogen bromide is an acidic product and serves to keep the bleach injector clean of calcium carbonate scale over time. If added in the correct proportions, the resulting pH will always be between 6.9 and 7.4, depending on the quality of the feed (dilution) water. Concentrations of 100–300 ppm as available bromine can be made very efficiently in this manner. The reaction time of bleach-bromide is usually <1–10 seconds,

depending on the pH. At pH of 7.2, the reaction is fast. The solution then should pass through an in-line mixing device of some kind, such as a static mixer, to assure efficiency of the reaction. The solutions may be heated to <120° F without any negative consequences. These concentrations (in cool or warm water) have little to no detectable odor.

3) Blend Tank Mixing:

Pre-mixing a concentrated solution in a mix tank could be a preferred method if multiple injection points are considered. This method of blending is acceptable and quite efficient. Cool water is required for any blend tank mixing operations, as hot or warm water accelerates the decomposition of hypobromous acid, which will depress the pH and will require excessive amounts of bleach to keep pH in the normal ranges.

The chemistry of hypobromous acid changes at higher concentrations (>2,000 ppm), however. The decay rate of hypobromous acid (HOBr) is directly proportional to the concentration of the HOBr in solution. As the concentration increases, the decay rate of the HOBr also increases, due to the product degrading back into hydrogen bromide. The pH drops and more HOBr reverts to hydrogen bromide (HBr), and then the pH drops more, and so on. Therefore, more bleach is necessary to keep the pH within range and slow the decay cycle.

This phenomenon can be controlled if one chooses to use higher concentrations (up to 4,500 ppm). Cycle times within the tank should be kept short to avoid degradation problems at these higher concentrations, which would require a smaller tank size; something in the <100 gal range. For example, a 4,500 ppm solution degraded by 10% in 15 minutes, which also would require significantly more bleach to re-activate the solution. This also related to a 1% drop in activity and slightly lower pH values within 5 minutes of activation. Please refer to the graphs presented below for further guidance.

In practice, one could choose to set the make-up water flow rate only slightly more than the exit water flow rate, which would keep the cycle time much shorter. Therefore, the pH depression effect is minimized, and a fresh solution is always available. Concentrate product in the range of 2,000–2,500 ppm would be the preferred target range, as it would have a much less tendency to decay over time, and the solutions would be stable over longer periods, such as breaks, lunches, equipment down-time, etc. Concentrations above 4,500 ppm are not recommended for most applications, as this appears to be the ceiling for reasonable operations in a processing facility.

Another advantage using lower concentrations would be shut-down and start-up considerations. If a tank that contained 3,500–4,500 ppm of hypobromous acid were to be left unattended over a weekend, the resulting solution on Monday morning would undoubtedly be orange in color (due to the presence of dissolved bromine that developed as a result of the pH depression). There may be some distinctive bromine odors and the user would have to add significant bleach to bring the

pH up to normal operating ranges before starting the system. Solutions in the 1,000–2,000 ppm range would not exhibit the same level of pH depression and would require much less bleach activation to bring it into range.

Typically, mixing devices are not necessary in a blend tank operation. The inflow water would be controlled by a level controller and water solenoid, which would also engage the hydrogen bromide and bleach pumps simultaneously. If the water supply is pressure regulated, the flow volume of the water into the tank would be consistent and constant, and the chemical injection pumps could be set at an established rate. This chemical feed rate should not change significantly so long as the pressure of the water inflow is consistent. The chemical feeds could be injected into the water line simultaneously or just prior to entering the blend tank, and the agitation that is created is sufficient to thoroughly mix the water and chemical solutions. Therefore, an external mixing device may not be necessary.

Blend tank “fill and mix” cycle times should be proportional to the solution’s strength. Cycle times should be chosen to achieve maximum conversion and efficiency with minimal pH effects. For concentrations greater than 2,000 ppm as available bromine, Enviro Tech has determined that holding times, considering the total blend tank residence and pipe travel times, should be in the range of 2–3.5 minutes total time. Again, the tank size and concentration of the solution chosen will dictate this cycle. Please review the pH graphs listed below to determine the operational parameters of your system, based on the concentration of the hypobromous acid solution you choose.

We are not endorsing any particular concentration for a blend tank method of mixing, nor are we discouraging higher concentrations of the HOBr. But each plant and operation is different and each location must make the decision what works best for their operation. Knowing the advantages and disadvantages of the different methods and concentrations is what is intended to be presented here.

4) The Chemistry of Testing:

Enviro Tech has established 2 test methods for the liquid hypobromous acid applications. There are very valid and significant reasons why there are 2 kits. Each one has their place and will be explained.

Most end-users prefer simple and reasonably accurate drop kit methodology to test chemical solutions. But there is no simple drop kit available that can distinguish chlorine from bromine. The problem is that chlorine, for use on meat, is basically worthless, but bromine is quite superior. The drop kit method only reports total bromine and chlorine. It is imperative that all solutions made in a blend tank or in-line methods contain verified bromine concentrations.

In response to the need to distinguish bromine from chlorine, Enviro Tech developed a “DPD Validation Method for Bromine

Solutions”. This method is very accurate and precise, and although it is more complicated than the “drop kit” method, it is still relatively easy to use.

a) Drop Kit Method: This method uses standard chemistry, which adds potassium iodide to a solution. Starch is added to give it a deep blue color. Then sodium thiosulfate is added dropwise until the solution turns clear. This is the endpoint, and each drop = 20 ppm as available bromine. This method cannot distinguish chlorine from bromine, and should only be used after the hypobromous acid solution is confirmed using the DPD Validation Method. This test can be used routinely for hourly or daily checks once the quality of the hypobromous acid solution is verified.

b) DPD Validation Method for Hypobromous Acid: This method is much more accurate than the drop kit method and it can distinguish between chlorine and bromine species. It uses a colorimeter which can only read a maximum of 5 ppm as bromine, so the solutions must be diluted into range before the test is run. It uses a pink indicator called DPD. The intensity of the pink color is determined by a small hand-held colorimeter. One test is performed on a test solution to establish the “total halogen”. Then a solution called glycine is added and the test is repeated. The glycine neutralizes the excess chlorine. So the first reading gives an amount for “total” chlorine plus bromine (TH), and after the glycine the reading is all bromine “B”. The second reading is subtracted from the first to establish the true available chlorine (“C”) content. If the readings are almost equal, then 100% of the halogen is bromine.

This testing methodology also is used to “balance” the reaction products made from blending hydrogen bromide with bleach. Once the system is operational, the test can confirm the amount of excess bleach.

Subsequently one should turn down the bleach pump(s) to obtain no more than about 5 ppm of free chlorine at the end-use dilution sampling location.

In the below graphs we present the reader with a basic picture of the efficiency of the hypobromous acid and hypochlorite reaction at various concentrations. Note that excess bleach (hypochlorite) was used in this series of experiments so one could also track the influence or presence of the excess chlorine over time, contrasted with the hypobromous acid (HOBr).

(5) Summary:

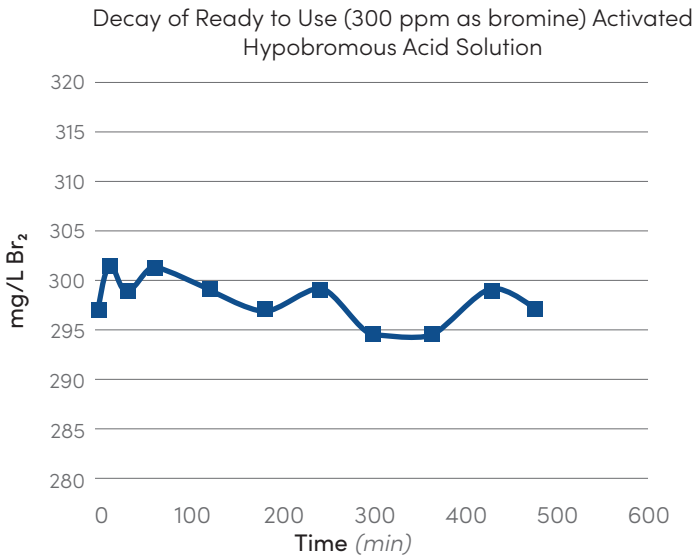
All solutions of 1,000 (and greater) ppm hypobromous acid degrade over relatively short time periods. Solutions of 1,000–2,000 ppm as hypobromous acid should be diluted and used within 1 minute of mixing.

However, solutions between 3,000 and 4,500 ppm as hypobromous acid do not “peak” until about 3 minutes

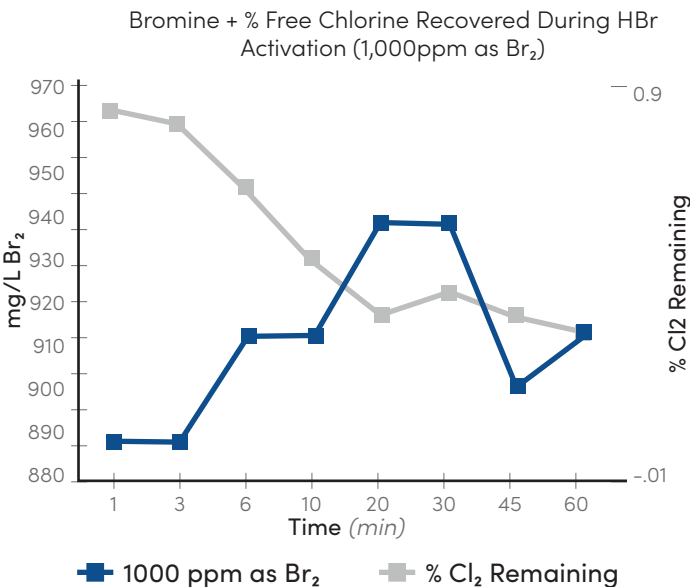
after blending. Therefore, one should incorporate these parameters when designing and operating the hypobromous acid methodology, in order to assure peak performance and optimization as well as obtain efficient economy of use.

NOTE: The following graphs were intentionally conducted using an excess of bleach (chlorine) to show the tendency of both species to decay over time.

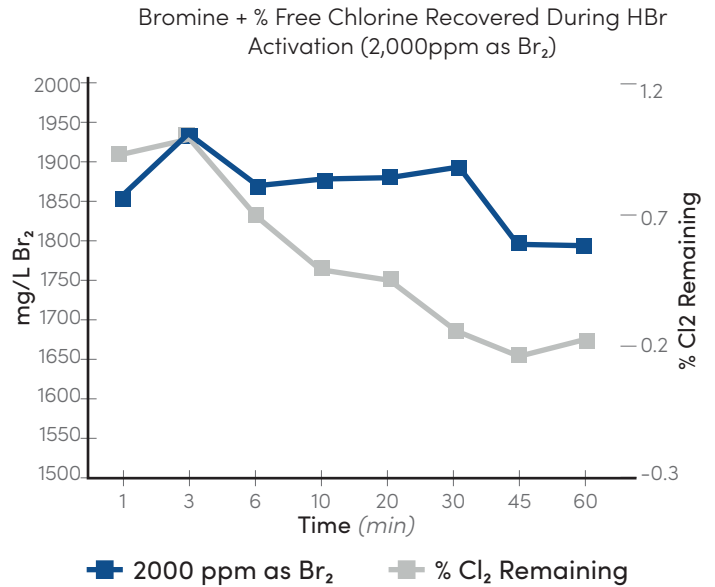
GRAPH 1 Stability of a RTU solution at 300 ppm as hypobromous acid



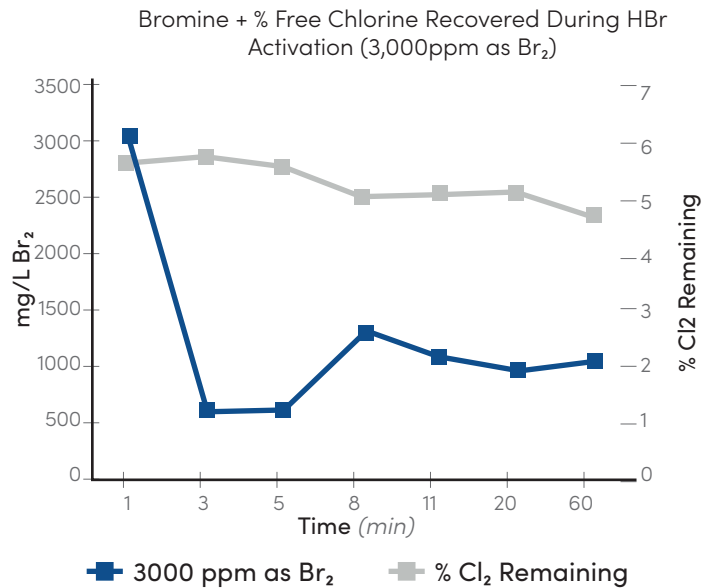
GRAPH 2: 1,000 ppm approximate target (with excess bleach) pH over 60 minutes rose from 7.57 to 7.68



GRAPH 3: 2,000 ppm approximate target (with excess bleach) pH over 60 minutes rose from 7.37 to 7.46



GRAPH 4: 3,000 ppm approximate target (with excess bleach) pH over 60 minutes rose from 7.5 to 7.2



**GRAPH 5: 4,400 ppm approximate target (with excess bleach)
pH over 60 minutes dropped from 7.5 to 7.1**

