The Power of Ozone in Pharma Process Water - V.Baratharaj

Category: Latest

New Delhi, March 15, 2016: Ozone is a very effective disinfectant/oxidant and is being preferred over other disinfectant technologies .The effectiveness of ozone is governed by its chemistry and this facilitates its use with other agents such as peroxides, UV for enhanced disinfectant/oxidative properties

Ozone Chemistry

Ozone is O3 and has both a single as well as a double bond inits chemical structure The single bond is weak and can form radicals . This is similar to peroxide structure. The double bond is stronger and comparable to the oxygen double bonds. This double bond is unreactive

Ozone exists as two resonance structure as below:

These two resonance structure are interchangeable and is so fast that ozone always exists in these two forms

Ozone Vs Oxygen as Oxidizing Agent - The concept of Oxidation state

Ozone is a more powerful oxidant even when compared to Oxygen. –Why

Each element has its own oxidation state in the structure . In water the oxidation state of hydrogen atom is +1 since it has yielded its electron to the oxygen atom. The oxidation state of oxygen in water is -2 because oxygen has one electron from each hydrogen atom

The usual oxidation state of oxygen is -2 . But in both ozone and oxygen the oxidation state is Zero . So both ozone and oxygen can draw electrons from a source and thereby decreasing the oxidation state of at least one oxygen atom in the process

Ozone is a more powerful oxidant than oxygen because ozone can readily react with a substrate on its own whereas oxygen cannot and may require a catalyst to initiate a reaction

The power of an oxidization agent is often is expressed in the form of oxidation reduction potential in Volts . Here is a comparison of the oxidation reduction potential of some of the commonly used oxidizing agents

Oxidizing Agent	EOP (volt)	EOP vs. Cl_2
Fluorine	3.06	2.25
Hydroxyl Radical	2.80	2.05
Oxygen (atomic)	2.42	1.78
OZONE	2.07	1.52
Hydrogen Peroxide	1.78	1.30
Hypochlorite	1.49	1.10
Chlorine	1.36	1.00
Chlorine Dioxide	1.27	0.93
Oxygen (molecular)	1.23	0.90

During the process of oxidation , Ozone releases O2 molecules and also one oxygen atom with the familiar oxidation state of -2 This process has a standard reduction potential of 2.07 V. Compare this with the reduction potential of other oxidizing agents you will note Ozone has a higher potential than most oxidizing agents meaning that the ability of ozone to oxidize most species is thermodynamically allowed.

How Ozone Works

The different chemical pathways are available for ozone oxidations . some pathways are relatively easy and proceeds fast(fast ozone reactions). Compounds containing multiple bonds (such as C=C, C=N, N=N, etc .have easy pathways and can proceed till mineralization (CO2 &H2O). Ozone does not react with single bond such as C-C, C-O, O-H at near the same rate as double bonds This is, because there is no easy chemical pathway for the oxidation to take place

However it is observed that such as S^{2-},which are simple oxidizable ions ,readily forms oxy anions such as SO_3^{2-} and SO_4^{2-}. These oxidations are simple and the mechanisms only require contact of ozone with the ion. The oxidation of these ions by ozone is very rapid

Ozone is capable of reacting with many compounds .However kinetic factors often determines whether ozone will react with the compound and oxidize it in quick time . An appropriate reaction pathway must be available for ozone to react with a compound. Thermodynamics may favor an ozone induced oxidation (because of high oxidation reduction potential) but, kinetic factors will most often dictate whether ozone will oxidize a compound in a reasonable time . This is the

main reason that we need to study the chemical composition of different compounds and determine whether it is economically possible to suggest ozone as a prime oxidant.

ADVANCED OXIDATION PROCESS (AOP)

Ozone reactions can be enhanced when it is combined with other agents such as H2O2 and UV . This process is known as advanced Oxidation process (commonly known as AOP). We have seen that the Electro potential of the OH radical (OH-)is higher than ozone at 2.80 V. Tpable of the use of AOP process are capable of reacting with many other compounds and at much greater speeds than with ozone alone . The AOP process will also facilitate total mineralization of an organic compound

Ultraviolet (UV) with ozone (AOP)

We must understand that the energy of UV light is on the same order as that of covalent bonds UV thus provides the energy to break chemical bonds . When ozone is used in combination the smaller broken compounds are further broken down by ozone and this will make the compound degrade further

UV is commonly used in this manner as an ozone "destruct,", converting ozone to molecular oxygen. Since UV can cause the conversion of ozone to molecular oxygen, But the wave length required is two to three times more than the wave length of UV required for oxidation /disinfectant.. It is proper to very carefully consider the location of the ozone in the process when using UV as, the conversion of ozone to molecular oxygen can retard the process

Hydrogen Peroxide (H_2O_2)

Hydrogen peroxide readily decomposes to OH- radicals (hydroxyl) and OH- radical are very reactive . This property is enhanced by UV light, by high temperatures and also by sunlight .Hydroxyl free radicals will attach and withdraw atoms from compounds and make them unstable .This compound will now be susceptible to ozone reactions

High pH

It is well known hat just as ozone exits in two resonance structure , in water ozone exists in both O3 molecular form and OH- radical forms . The proportion of OH- and O3 molecular will depend on the pH . At low acidic pH the molecular form ozone will dominate . As the pH increases, the radical form OH- will start increasing with very little molecular ozone present above pH 8.5-9.0. the actual route is the conversion of ozone to Hydrogen peroxide at high pH which is the primary source of OH- radicals

Disinfectant property Vs oxidizing property of ozone.

Molecular ozone has a far better disinfectant property than OH- radicals .Hence thee presence of more molecular ozone at low pH means there is a higher disinfectant property. and the presence of more OH radicals means better oxidation actions of ozone . For proper disinfectant activity of ozone the pH should be below 8.0

Ozone dose, Ozone Contact time – importance in Pharma process

The use of chlorine in pharma process water has been used for ages now. It is still the preferred disinfectant and most economical . The problem with both Chlorine (as well as UV) , we do not have any methods of on line measurement of the level of disinfectant property. In many cases chlorine is very unreliable because of the emergence of resistant strains, emergence of mutant strains of commonly occurring Bacilli especially gram negative pathogens. A higher dose and higher contact time also may not produce required quality plus you run the risk of THM formation in the water

The use of ozone provides a reliable method of online measurements. With proper design of ozone dose and sufficient contact time, you are almost certain that 10 out of 10 times you achieve the quality required. The residual ozone measurement on line will

indicate the levels for control of the whole process.

How do you ensure this ?

The presence of ozone residual for a minimum period of 15 minutes have been proven to produce excellent results in Phrama process water treatment. However, control of this process assumes importance, especially with regards to the required ozone residual and the required contact time .The design of the system must ensure this and make it fool proof .. The following aspects need to be checked & ensured

Ozonator must be reliable and produce the required ozone and this must be tested and guaranteed by the supplier. This is important as Industry has never been kind to ozone manufacturers in India in view of their inability to guarantee t ozone production they claim for their machines
Feed gas must only be oxygen to obtain ozone at high concentration
The venturi and the pump must be selected based on the process requirement and backed up by performance curves . Locally fabricated venturis must not be used
For an on line process the contact time must be controlled by using level controllers
The ozone residual must be checked during ozonation , at storage levels, and after ozone destruction to ensure full control of the process

Suggested ozone residuals: Ideally when you measure ozone residuals in the water, you can expect that a good design will achieve the following minimum levels:

Immediately after ozonation: 7 – 1.2 ppm
In ozonation tank : 0.1-0.2 ppm
In storage tanks after ozonation tank : 0.05 -0.1 ppm
After UV destruction: Zero
At sampling points before ozone destruction

1. **Before storage tank : 0.1-0.2 ppm**

2. **After ozone tank : depending on storage tank size and usage : 0.05 ppm . (this is a tough ask) since accurate measurements are not always possible as they are invariably checked with potable instruments whose accuracy is only up to 75-80%**

Tank Cleaning a MUST

An ozone system provides pure water only to the extent the tanks and the entire loop of water distribution are kept disinfected and clean. The storage tanks can be another source of recontamination of ozonated water. The tanks need to be cleaned and disinfected so that you do not run the risk of re-contamination . The larger the tank, the more difficult this becomes. Maintaining small residual ozone by design of the ozone system could help in this process..The water should be stripped ozone just before use . This is a very good practice

All pipes in the distribution system can be cleaned by using ozone effectively. ozone is a good agent to remove bio-fouling layers but not really suitable to clean membranes of RO/UF . There are different school of thoughts regarding the use of little ozone to clean RO membranes. Since the effect of membranes are dose and contact time related a small amount of ozone of 0.05 ppm in the water have been used for cleaning of membranes. This process has not be authenticated and may be considered as a risk detailed studies provide otherwise.

Corporate Comm India(CCI Newswire)