CONCEPT/POSITION PAPER ON FERRATE (VI)

By
Thomas D. Waite, Ph.D., P.E.

What is a Ferrate?

Iron in its familiar form exists in the + 2 and + 3 oxidation states. However, it is possible to obtain higher oxidation states of iron because it is a transition metal. In fact, theoretically valances up to + 8 can be generated. These high valance iron states are usually generated as oxyanions of iron, called ferrates, and the most stable valence is (+6) or (FeO_4^{2-}). In this case the valance of iron is + 6 and the compound is referred to as Ferrate (VI). Ferrate (VI) has a dark purple color similar to permanganate (MnO_4^{2-}) but behaves much differently in all respects.

Ferrates have been studied extensively at least since 1841, when Fremy first synthesized potassium ferrate ($K_2FeO_4^2$). Since that time volumes of literature have been generated describing ferrate structure, behavior and reaction potential in many system.

Oxidation Capacity

Ferrate (VI) is perhaps the most powerful oxidizing compound that can be utilized in normal applications, with an oxidation potential of 2.2 volts under acid conditions. This potential can be compared to ozone (O_3) that has an oxidation potential of 2.04 volts, and chlorine which has a potential of approximately 1.4 volts. Therefore, in most oxidation reactions, Ferrate (VI) will be the most powerful chemical that can be utilized.

Disinfection Capacity

An extensive amount of work has been published since the early 70's on the utilization of Ferrate (VI) for disinfecting water and wastewater systems. Ferrate (VI) has been repeatedly shown to be an extremely efficient biocide in all cases, including an

effective demonstration as an anti-biofouling treatment chemical. Studies have shown that Ferrate (VI) can easily reduce the concentration of enteric microorganisms by over 3 logs in a few minutes at concentration in the ppm range. Ferrate (VI) has also been demonstrated to inactive organisms e.g. *Cryptosporidium* that are not easily inactivated by other general disinfectants such as chlorine. In recent studies utilizing Ferrate (VI) for treatment of domestic wastewater sludge, indicator organisms such as coliforms and salmonella were reduced to below detection at even moderate doses of the treatment chemical.

Coagulation Capacity

The stable decomposition product of Ferrate (VI) is iron in either the + 2 or + 3 oxidation state. Iron, of course, is one of the most common elements on this planet, and is not only non-toxic but in fact is required as a growth factor by humans. In addition, ferric and ferrous irons are utilized widely as coagulants to remove suspended solids from aqueous systems. Therefore, once Ferrate (VI) has expended its oxidation power, it is quickly reduced to an iron matrix that is then capable of coagulating suspended solids, increasing the purity of the water or wastewater being treated. This means that by the addition of just Ferrate (VI) alone, treatment equivalent to a combination of common water and wastewater treatments, is achieved. In addition to coagulating suspended materials, the solid ferric and ferrous compounds generated from Ferrate (VI) addition have been shown to be extremely effective at co-precipitating and absorbing dissolved metals from wastestreams. In fact a Ferrate (VI) process has been patented and utilized as an effective treatment means for removing uranium and transuranic elements from wastestreams. Because of its unmatched efficiency at co-precipitating metals from

solution, the residual after treatment (sludge) is less than half that generated by conventional precipitation procedures. Considering that the sludge generated from these processes is considered a toxic material, sludge generation becomes a critical factor in design; and savings in sludge generation become a major motivating force in selection of treatment chemicals. In this regard, Ferrate (VI) has been demonstrated at Los Alamos, National Labs, West Valley Nuclear Services, and at the Rocky Flats Nuclear Facilities, to treat water from low-level radioactive waste treatment facilities. In all cases Ferrate (VI) reduced the level of gross alpha and beta reactivity while generating less than half of the sludge typical of treatment facilities for treating this waste.

Application to General Water and Wastewater Treatment Systems

Ferrate (VI) has been demonstrated to be effective treatment chemical in all sorts of water and wastewater systems. Ferrate (VI) has been demonstrated to completely treat drinking water, which is removing indicator bacteria and suspened solids, by simple addition ahead of a media filter. This direct filtration process demonstrated that Ferrate (VI) could simply be added to a water treatment scheme without the need for an expensive and large infrastructure normally required to coagulate and precipitate residuals. In addition, it has been demonstrated that by utilizing Ferrate (VI) for routine oxidation and disinfection processes within a water treatment plant, that the formation of disinfection by-products, such as trihalomethanes (THMs) are precluded. In fact, published research has shown that no THMs are formed when Ferrate (VI) is utilized in a water treatment process. It is postulated that by utilizing Ferrate (VI) for all of the various oxidation and coagulation treatment processes required in a treatment plant, very

little precursor residual would remain, such that, an addition of a chlorine residual for distribution in the pipelines could be easily achieved with no THM formation.

Ferrate (VI) has also been shown to be extremely effective at disinfecting effluents from secondary waste treatment plants for safe discharge to the environment. In addition, no toxic residuals were generated, so that toxicity requirements for effluent discharges are not violated.

Recent work has demonstrated that Ferrate (VI) can be added to digested sludge to facilitate treatment required for the generation of a class A biosolids. It has been clearly shown that Ferrate (VI), because of its unique properties, can rapidly disinfect all organisms associated with the biosolids, and can oxidize all reduced carbon and sulfur compounds, thereby eliminating odors. Also, because Ferrate (VI) degradation products are innocuous ferric hydroxides, the sludge can be easily dewatered (measured @ 43% solids), with the result being that a high quality bio-solids product is formed simply by the addition of the Ferrate (VI) prior to mechanical dewatering systems.

The above is a brief summary of the documented and published information concerning application of Ferrate (VI) for various treatment schemes. An exhaustive review of all of the Ferrate (VI) application literature is beyond the scope of this evaluation, but it should be clear to the reader that an enormous amount of documented and published work exists defining the efficacy of Ferrate (VI) treatment for all aspects of water, wastewater and industrial scenarios. In fact, many studies have been undertaken within industries to examine the effects of Ferrate (VI) on their unique wastestreams; while most of this material remains proprietary within the industries, a large market undoubtedly also exists in this area.

Why has Ferrate (VI) not Been Used?

As noted above, all ferrate compounds are relatively unstable because of their high valance. In fact, the most stable of the ferrates (FeO_4^{2-}), is only stable in caustic solutions or at a very high pH. The fundamental issue effecting generation of ferrate compounds is this lack of stability as well as the solubility relationships of the ferrate compounds synthesized. It is a fairly simple task to oxidize iron to a + 6 valance state in a caustic medium however, at that point separation and purification processes become extremely expensive. In addition, it is difficult to stabilize the end product long enough to have it considered as a saleable bulk chemical. Solid ferrate compounds such as K_2FeO_4 require special handling in order to prevent rapid decomposition to ferric iron. Solutions of Ferrate (VI) such as $Na_2FeO_4^2$ require large concentrations of caustic for stability. Several commercial attempts have been made to generate reasonably priced Ferrate (VI) compounds, but to date all have failed. The most recent attempt was the synthesis of K_2FeO_4 called TRUE/CLEAR and the product became available for $35 lb., which was far too expensive for general use.

It is clear that while Ferrate (VI) appears to be an efficient treatment chemical for all aspects of industrial processing and environmental applications, its cost must be reduced to a point where it can compete with current treatment chemicals and processes. In addition, issues associated with transport, storage and stability of ferrate compounds must be addressed in order to make this a workable treatment scenario. The result of all of these complications is that Ferrate (VI) compounds have not been utilized on any scale to date for industrial processes.

Solution to the Ferrate "Problem"

Ab Initio, LC is poised to demonstrate a solution to the dilemma that has kept Ferrate (VI) from being available to all industrial and municipal markets at a low price, and in bulk quantities. They approached the problem in a totally different manner than previous attempts at manufacturing Ferrate (VI), i.e. they envisioned a process where a Ferrate (VI) product could be readily produced on site utilizing typical bulk chemical feeds. This unique thought process led a design of a system that could be readily implemented for any scenario, and produce large volumes of a Ferrate (VI) product at extremely low prices. After two years of development work, Ab Initio, LC developed and refined the chemistry for the generation of this product and this patent-applied-for process is now being fabricated in prototype facilities, which will be demonstrated by the summer of 2002. Preliminary estimates indicate that this process will be able to develop a Ferrate (VI) product for less than $1/10^{th}$ the cost of any previous product. In addition, this unique system will allow for incorporation of this technology into any existing treatment facility, or for utilization in areas where mobility or modular systems are required. It is anticipated that because of this breakthrough in chemistry and process design, that a powerful Ferrate (VI) product will soon be available to take advantage of over 150 years of research demonstrating the efficacy of this compound for many applications.