

# Accelerated Ferrous Oxidation with a Multiple Orifice Spray Reactor

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## **Abstract:**

A bench scale experiment using a multiple orifice spray reactor was investigated as a potential remediation technology for the rapid oxidation of ferrous iron in acidic mine discharges. The orifice spray reactor makes use of flow through multiple orifices to enhance aqueous aeration and oxidation rates. The reactor consists of two concentric cylinders, the inner cylinder having a series of orifices which act in a manner similar to a venturi. In this fashion neutralization and aeration are combined into a single step due to the aspiration of air and dispensing of alkaline agents into the reaction chamber.

Results show ferrous iron oxidation rates at pH values between 6 and 7 can be increased by four orders of magnitude as compared to literature obtained oxidation rates. At an influent ferrous iron concentration of around 150 mg/L and pH of 6, the orifice spray reactor can achieve conversions of ferrous to ferric iron of about 30% within one second. Under certain conditions, the orifice spray reactor oxidizes more ferrous iron than can be simply attributed to the oxygen transfer capabilities of the system. It is suggested that the oxidation capability in excess of oxygen transfer is due to, or initiated by, the effects of hydrodynamic cavitation.

**Narrative:**

The objective of this research is to explore the abilities of a multiple orifice spray reactor (MOSR), an alternative active treatment device for active remediation sites that offers opportunities of rapid iron oxidation while requiring a small “footprint” of land space. The scope of this paper is to present data and information regarding enhanced ferrous iron oxidation resulting from a bench scale multiple orifice spray reactor.

It is known that when flow enters a sharp edged orifice, the flow detaches from the sides of the orifice and forms a vena contracta. The contraction at the inlet sufficiently reduces the cross sectional area of the flow. This reduced flow area results in a localized increase in liquid velocity and subsequent pressure drop. If the absolute pressure falls below the vapor pressure of the liquid then cavitation results with vapor cavities forming within the bulk fluid. Tseng and Collicott (2000) report that cavitation in an orifice is almost always present in flow through an orifice at and downstream of the inlet hole, and has been demonstrated from 4 psi to 30,458 psi (30 KPa to 210 MPa). As the pressure in the bulk liquid recovers, these cavities rapidly collapse. In the case of the MOSR, the recovered pressure (outlet) is approximately equal to atmospheric.

One way to assess the occurrence of cavitation in fluid flow through an orifice is through the use of Bernoulli's equation. From Bernoulli's equation, a dimensionless cavitation number,  $\sigma$ , can be derived which measures the resistance of flow to cavitation. The cavitation number,  $\sigma$ , is deduced from the relation between static pressure,  $P$ , and flow

velocity,  $u$ . Bernoulli's equation states that the pressure drops due to flow are proportional to the product of fluid density and the square root of the flow velocity.

The cavitation number  $\sigma$  is obtained by dividing the available static pressure,  $P_0 - P_v$ , by the dynamic flow pressure (Shah et al. 1999):

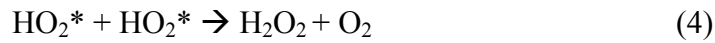
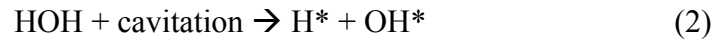
$$\sigma = \frac{P_0 - P_v}{\frac{1}{2} \rho u^2} \quad (1)$$

Where  $P_0$  is the ambient pressure or pressure downstream of the orifice,  $P_v$  is the vapor pressure of the fluid flowing through the orifice,  $\rho$  is the liquid density, and  $u$  is the liquid velocity through the orifice. The particular value at which cavitation is incipient is termed the “cavitation inception number”. Under ideal conditions, cavitation usually occurs for  $\sigma < 1$ , all though cavitation inception can occur at cavitation number values greater than and less than 1. Factors affecting cavitation inception are the geometry of the orifice and the presence of dissolved species and gases. Dissolved species including dissolved gases produce weak spots in the fluid continuum for cavities to form, thus enhancing the cavitation process.

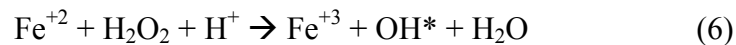
When cavities collapse, localities of high temperature and pressure exist. This can enhance chemical oxidation reactions. In addition, the generation of local high temperatures and pressures induces the cleavage of water molecules and results in the formation of free radicals such as  $\text{OH}^*$ . Free radicals such as  $\text{OH}^*$  have very strong oxidizing capabilities which may further oxidize ferrous iron. Strong oxidizing abilities generated by cavitation was reported by Kumar et al. (2000), who used flow through an

orifice plate to induce bacteria oxidation and inactivation. It is likely that the observations of enhanced iron oxidation by Ackman and Kleinmann (1984) are due to oxidants being produced as a consequence of cavitation which can take place inside a venturi as well as in an orifice.

Cavitation conditions can produce OH\* and peroxides in accord with the following equations:



Any H<sub>2</sub>O<sub>2</sub> produced may additionally react with ferrous iron resulting in the actual quantity of ferrous iron oxidation being greater within a cavitating reactor than can be explained by oxygen transfer alone. The reaction of Fe<sup>+2</sup> with H<sub>2</sub>O<sub>2</sub> is known in as Fenton's Reaction and is represented stoichiometrically as (Stumm and Morgan 1996):



Thus, the total production of OH\* radicals would be from the cleavage of the water molecule due to cavitation plus from the reaction of any intermediate-produced H<sub>2</sub>O<sub>2</sub> with ferrous iron as shown in equation 6.

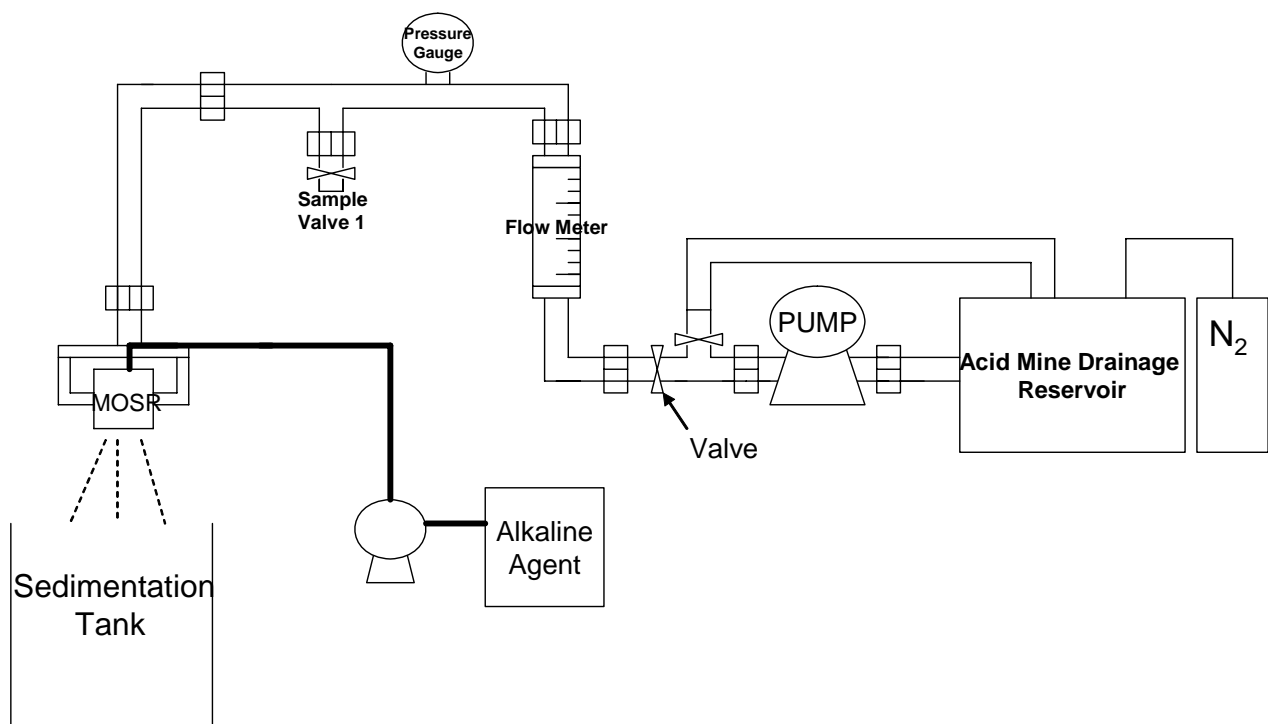
The following data and information with the MOSR suggests enhanced overall ferrous iron oxidation beyond that explained by simple atmospheric oxygen transfer.

### **Methods and Data Summary**

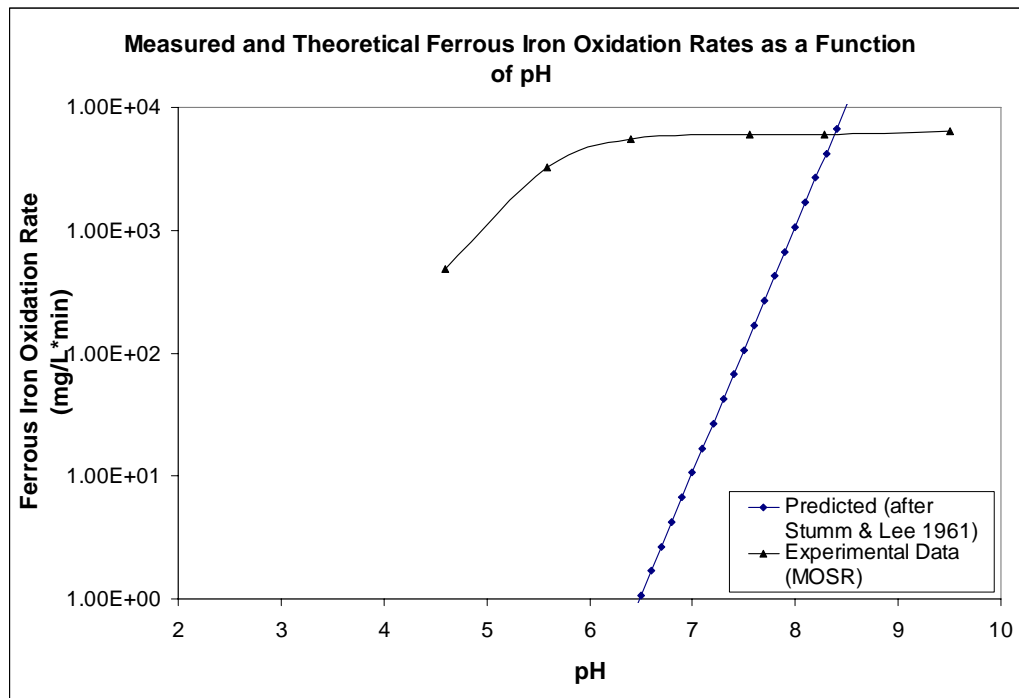
Figure 1 is a schematic flow diagram of the bench scale MOSR high rate oxidation system. Inlet pressures were varied to a maximum of about 70 psi (limited only by the nature of the plastic piping system used), and NaOH addition was controlled manually so that the effluent pH was a predetermined levels. Further experimental details are reported by Klein and Neufeld (2005).

Figure 2 compares the theoretical rate of ferrous iron oxidation at various pH values as reported in the literature with measured values when using the MOSR bench scale apparatus. These results suggest that the multiple orifice spray reactor (MOSR), consisting of multiple orifices within an annulus, is an effective approach for the treatment of ferrous containing mine drainage. At pH values in the range of 6 to 7, the rate of ferrous iron conversion appears to be about 4+ orders of magnitude greater than that expected by conventional aeration. This advantage is diminished as the residual pH value is maintained above 8, however, the potential savings in needed alkaline agent is apparent if the pH is maintained at lower values.

**Figure 1: Experimental Apparatus**



**Figure 2: Iron Oxidation Kinetics using the Experimental Apparatus**



## References

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## Acknowledgements

This project was made possible with financial support from the Southern Alleghenies Conservancy, the PA Department of Environmental Protection Resource Recovery Consortium, and the Fraunhofer Center for Energy and the Environment. Special thanks go to F<sup>2</sup> Machine Shop, Tarentum, PA, and PPC Corporation, Pittsburgh, PA the fabricators of the bench scale orifice spray reactor.