

## PEROXYBORATE AS A DECONTAMINATION AGENT

Beverly Ausmus Ramsey, PhD  
Vice President  
Systematic Management Services  
Germantown, MD 20874

### ABSTRACT

The use of peroxyborate  $[(\text{OH}_2)\text{B}(\text{O}_2)_2\text{B}(\text{OH})_2]^{-2}$  in selected decontamination, outage, and waste container treatment operations offers an interesting alternative to existing agents. Its application as sodium peroxyborate also offers additional benefits, especially in decontamination efforts for Safestor or cold standby layup. The attributes the superoxidizer, sodium peroxyborate, include:

- Neither sodium ions nor peroxyborate ions nor any breakdown products are RCRA characteristic or listed hazardous wastes;
- The stable degradation products, NaOH, sodium borate and water are residuals which have no lasting physicochemical effect on materials contacted;
- The solution can be used as input to recycle or recovery unit operations for selected metals or radionuclides;
- The solution removes and flushes corrosion products;
- Its application decomposes many organics;
- It is a powerful biocide, attacking microorganisms in solution and on surfaces; and
- A principal breakdown product, sodium borate, is a corrosion inhibitor.

Peroxyborate, as sodium peroxyborate, was used in the Three Mile Island Unit II Reactor Coolant System, the Spent Fuel Pool, in stainless steel radwaste tanks, and for disinfection of the fuel canisters filled with debris which were subsequently shipped to INEL for long-term storage. Lessons learned from these applications included the utility of sodium peroxyborate for: 1) flushing steam generator tubes as a layup procedure to prevent microbially induced corrosion (MIC) during extended outages, 2) treatment of stainless steel waste containers prior to geologic emplacement to minimize the risk of MIC; and 3) destruction of organic contaminants in mixed wastes prior to radwaste treatment or waste solidification.

The use of peroxyborate as a superoxidizer should present a highly beneficial, low risk agent for specific decontamination applications during decommissioning as well as during waste package preparation for WIPP or repository emplacement and in outage or layup preparation procedures.

### STATEMENT OF THE PROBLEM

Much of the emphasis to date on decontamination methodologies has been on cleaning of concrete and steel surfaces as a prelude to or following dismantlement of plant systems. The use of most decontamination agents is accompanied by one or more of the following disadvantages: 1) the decontamination agent is a RCRA listed substance or meets the RCRA defined characteristics as toxic, etc.; 2) waste volumes are substantially increased; 3) no recycle, recovery process is applicable to the resulting wastes; 4) resulting wastes present equal or greater risks to workers, public health or environmental quality as the original materials; and/or 5) resulting wastes are not amenable to treatments which greatly reduce volumes.

The experience with D&D has largely focused on 1) solid media, 2) abiotic conditions, and 3) inorganic chemical reactions. As waste management costs become increasingly large components of project costs, the need to identify decontamination agents which can be applied to a variety of media and chemical conditions increases. Finally, new decontamination agents need to be selected based on waste minimization principles and be non-RCRA materials.

### CHARACTERISTICS OF PEROXYBORATE

Peroxyborate  $[(\text{OH}_2)\text{B}(\text{O}_2)_2\text{B}(\text{OH})_2]^{-2}$  is a strong oxidant and highly soluble anion. The anion is often formed with sodium and has been used extensively in the detergent industry for its oxidizing properties. Figure 1 shows the x-ray revealed crystal structure of the cyclic peroxyborate anion (1). There are at least two peroxyborate species present in solution, differing in thermal stability and solubility slightly.

In the presence of boric acid and sodium hydroxide, especially around a neutral pH, the addition of hydrogen peroxide yields peroxyborates and borate peroxyhydrates. These compounds are mostly chemically inert toward non-oxidizing acids and stable in air up to fairly high temperatures,

Peroxides, especially hydrogen peroxide, has been known as a disinfectant for many years (2-32). Peroxyborates, because of their superoxidizing power, are even more effective disinfectants under most conditions (4,8,9,10,12,15,21,23,24,27).

Peroxyborates, via hydroxy radical formation, seem to increase the solubilization of metals and specific cations, including sodium (33-37). Indeed, the solubility of some anions are affected by peroxyborates and peroxides (33).

Finally, peroxyborates stimulate degradation of organic compounds to more simple compounds (38,39).

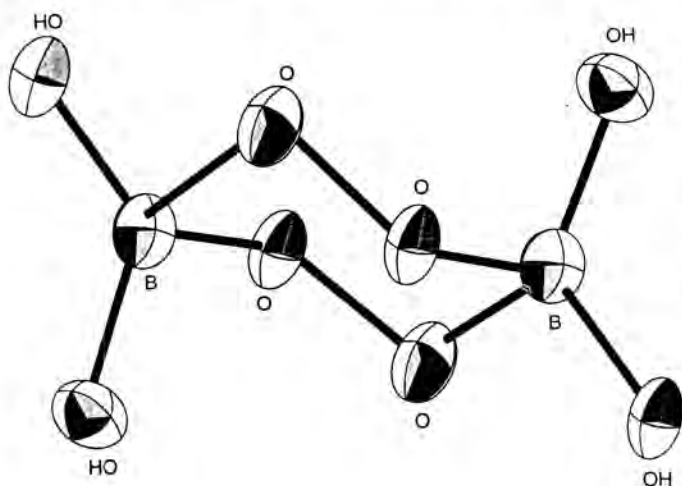


Fig. 1. Structure of the cyclic  $[B_2(O_2)_2(OH_4)_2]$ -anion.

Superoxidation is known to degrade organic compounds, including chlorinated solvents and pesticides (39).

#### PRELIMINARY DATE ON PEROXYBORATE AS A DECONTAMINATION AGENT

Peroxyborate formed in the reactor coolant system (RCS) of the Three Mile Island II damaged reactor was the agent used for its disinfection in 1986 during decommissioning. Peroxyborate was formed in the RCS by the addition of hydrogen peroxide to a highly buffered coolant consisting primarily of boric acid and sodium hydroxide. Its application as a disinfectant was made in response to the need to clarify the RCS coolant allowing the underwater cameras to be used to guide defueling tools applied to the damaged reactor core (40,41). The microbial outbreak in the RCS resulted from the use of ion exchange treated water from the basement of the TMI II containment building as makeup water. The water had been pumped into the basement as an emergency action during the TMI II accident in 1979, and contained microflora and microfauna characteristic of the source Susquehanna River.

Peroxyborate formed by the addition of hydrogen peroxide to the existing coolant fluid of boric acid and sodium hydroxide was also used in the Spent Fuel Pool, in stainless steel radwaste tanks, and for disinfection of the fuel canisters filled with debris which were subsequently shipped to INEL for long-term storage (42).

Lessons learned from these applications included the utility of sodium peroxyborate for:

1. Flushing steam generator tubes as a layup procedure to prevent microbially induced corrosion (MIC) during extended outages (46);
2. Treatment of stainless steel waste containers prior to geologic emplacement to minimize the risk of MIC; and
3. Destruction of organic contaminants in mixed wastes prior to radwaste treatment or waste solidification.

The formation of peroxyborate was hypothesized because complete disinfection was achieved by the addition of hydrogen peroxide at 200 ppm in the reactor coolant. This concentration of hydrogen peroxide is much less that would achieve

even partial disinfection. However, the addition of even this small concentration to the highly buffered sodium hydroxide and boric acid coolant (40) created a powerful oxidant which lysed all bacterial, algal and fungal cells encountered on surfaces and in the fluid (43,44).

Other effects on the reactor coolant system were noted as a function of the peroxide addition and peroxyborate formation (also reported in other studies:47-53). Figure 2 shows some of these effects, specifically the increase insoluble fractions of iron and silver, total alpha activity and organic carbon (45). The total organic carbon also was reduced, the range of the reduction was from 10 - 50% of the pretreatment concentrations.

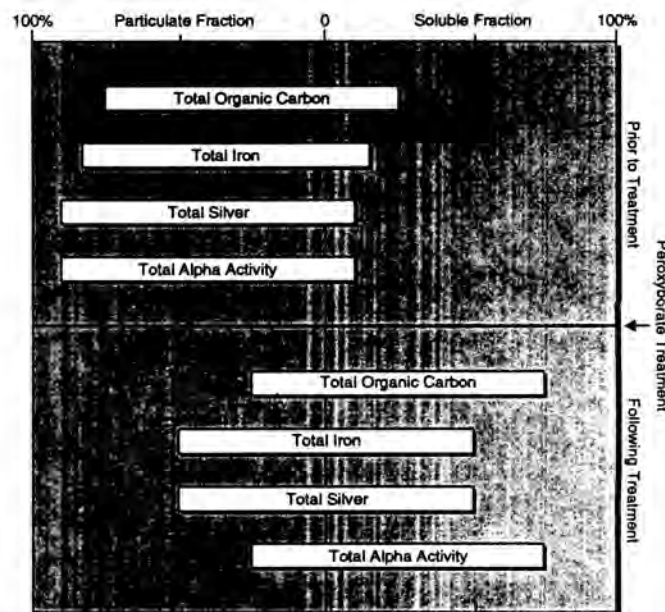


Fig. 2. Changes in soluble versus particulate fractions of TOC, Fe, Ag and Alpha as a function of Peroxyborate addition.

#### ADVANTAGES/DISADVANTAGES OF USING PEROXYBORATE

There are several advantages in the use of peroxyborate as a decontamination agent. These include:

- Can be used on surfaces and in aqueous media;
- Solubilizes metals and organics allowing recovery via physical or chemical means;
- Degrades organics, potentially could detoxify some wastestreams;
- Disinfects, reducing the possibility of microbially induced corrosion;
- Is not RCRA listed;
- Acts as a corrosion inhibitor;
- Degrades to non-RCRA listed or characteristic wastes; and
- Degrades in 2-8 hours, leaving no residues.

The disadvantages are relatively few:

- R&D needed to document efficacy and treatment rates
- Requires soluble treatment for metals recovery rather than filtration

- Most effective in solutions at pH 5-9
- May require repeated treatment/makeup because of time degradation to water, boric acid and dissociated sodium hydroxide

#### NEXT STEPS

There are several steps which need to be undertaken in order to bring peroxyborate into common use as a decontamination agent. These include:

- Testing efficacy for contaminant removal from concrete surfaces and other porous media
- Determination of solubilization rates for transuranics, metals and organics
- Testing as a flushing agent prior to system layup for MIC prevention

#### REFERENCES

1. WILLIAM D. GRIFFIN, ANDRZEJ C. SKAPSKI, and ANTHONY P. WEST, "X-Ray Crystal Structure of 'NaBO<sub>3</sub>-3H<sub>2</sub>O'; a Form of Sodium Perborate with Potential Applications in the Detergent Industry," *Chemistry and Industry* 5:185-186 (March 1984).
2. F.J. TURNER, "Hydrogen Peroxide and Other Oxidant Disinfectants," *Disinfection, Sterilization and Preservation* (Editor: Seymour S. Block) pages 240-250, (1983)
3. AHMED, F.I.K., and RUSSELL, C. 1975. Synergism between ultrasonic waves and hydrogen peroxide in the killing of microorganisms. *J. Appl. Bacteriol.*, 39, 31-40.
4. BABIOR, B.M. 1978. Oxygen-dependent microbial killing by phagocytes. *M. Engl. J. Med.*, 298, 659-668.
5. BAILEY, P.S., 1975. Reactivity of ozone with various organic functional groups important to water purification. In *Int. Symp. Ozone Water Wastewater Treatment. Proc.*, 1st 1973. Edited by R.G. Rice and M.E. Browning. Waterbury, Conn. Int. Ozone Inst., pp. 101-119.
6. BAYLISS, C.E., and WAITES, W.M. 1976. The effect of hydrogen peroxide on spores of *Clostridium bifermentans*. *J. Gen. Microbiol.*, 96, 401-407.
7. BLATTER, M. 1971. Apparatus and method for treating liquid substances polluted by microorganisms. *Fr. Demande* 2,068,597.
8. BOCK, F.G., MYERS, H.K., and FOX H.W. 1975. Cocarcinogenic activity of peroxy compounds. *J. Natl. Cancer Inst.*, 55, 1359-1361.
9. COHEN, G., and HEIKKILA, R.E. 1974. The generation of hydrogen peroxide, superoxide radical and hydroxyl radical by 6-hydroxydopamine, dialuric acid, and related cytotoxic agents. *J. Biol. Chem.*, 249, 2447-2452.
10. FRIDOVICH, I. 1978. The biology of oxygen radicals. *Science*, 201, 875-879.
11. FRIDOVICH, I. 1975. Oxygen: Boon and bane, *Am. Sci.*, 63, 54-60.
12. GUMP, W. 1979. Disinfectants and antiseptics. In *Kirk-Othmer Encyclopedia of Chemical Technology. Volume 7. Edited by M. Grayson and D. Eckroth.* New York, Wiley-Interscience, p. 807.
13. GUZMANN-BARRON, E.S., SEKI, L., and JOHNSON, P. 1952. Effect of hydrogen peroxide on cell metabolism, enzymes and proteins. *Arch. Biochem. Biophys.*, 41, 188-202.
14. HABER, F., and WEISS, J. 1934. The catalytic decomposition of hydrogen peroxide by iron salts. *Proc. R. Soc. Lond. Ser. A.*, 147, 332-351.
15. HALLIWELL, B. 1978. Biochemical mechanisms accounting for the toxic action of oxygen on living organisms: The key role of superoxide dismutase. *Cell Biol. Int. Rep.*, 2, 113-128.
16. HEINEMANN, P.G. 1913. The germicidal efficiency of commercial preparations of hydrogen peroxide. *JAMA*, 60, 1603-1606.
17. KING, W.L., and GOULD, G.W. 1969. Lysis of bacterial spores with hydrogen peroxide. *J. Appl. Bacteriol.*, 32, 481-490.
18. MENDEL, R., and SCHMIDT, J. 1973. Investigations on rhinovirus inactivation by hydrogen peroxide. *Acta Virol.*, 17, 351-354.
19. MILLER, T.E. 1969. Killing and lysis of gram-negative bacteria through the synergistic effect of hydrogen peroxide, ascorbic acid and lysosome. *J. Bacteriol.*, 98, 949-950.
20. NAGUIB, K., and HUSSEIN, L. 1972. The effect of hydrogen peroxide on the bacteriological quality and nutritive value of milk. *Milchwissenschaft*, 27, 758-762.
21. PELOUX, Y., NOFRE, C., CIER, A., and COLOBERT, L. 1962. Poliovirus inactivation by means of chemical systems productive of free hydroxyl radicals: Mechanism of the virucidal activity of hydrogen peroxide and of ascorbic acid. *Ann. Inst. Pasteur*, 102, 6-23
22. ROSENSWEIG, A.L. 1978. Hydrogen peroxide in prevention of water contamination. *Lancet*, 8070, 944.
23. SATTERFIELD, C.N. 1973. Peroxides. In *The Encyclopedia of Chemistry. 3rd Edition.* Edited by C.A. Hampel and G.G. Howley, New York, Van Nostrand Reinhold Co., pp. 813-816
24. SCHUMB, W.C., SATTERFIELD, C.N., and WENTWORTH, R.F. 1955. In *Hydrogen Peroxide.* New York, Reinhold Publishing Corp., pp. 515-547.
25. SMITH, W.W., and BODKIN, R.F. 1944. Influence of hydrogen ion concentration on the bactericidal action of ozone and chlorine, *J. Bacteriol.*, 47, 445 (Abstract).
26. SWARTLING, P., and LINDGREN, B. 1968. The sterilizing effect against *Bacillus subtilis* spores of hydrogen peroxide at different temperatures and concentrations. *J. Dairy Res.*, 35, 423-428.
27. SYMONYAN, M.A., and NALBANDYAN, R.M. 1979. Generation of superoxide radicals in alkaline solutions of hydrogen peroxide and the effect of superoxide dismutase on this system. *Biochim. Biophys. Acts*, 583, 279-286.
28. TOLEDO, R.T., ESCHER, F.E., and AYERS, J.C. 1973. Sporicidal properties of hydrogen peroxide against food spoilage organisms. *Appl. Microbiol.*, 26, 592-597.
29. WAITES, W.M., BAYLISS, C.E., KING, N.R., and DAVIES, A.M.C. 1979. The effect of transition metal ions on the resistance of bacterial spores to hydrogen peroxide and to heat. *J. Gen. Microbiol.*, 112, 225-233.

30. WARDLE, M.D., and RENNINGER, G.M. 1975. Biotic effect of hydrogen peroxide in spacecraft bacterial isolates. *Appl. Microbiol.*, 30, 710-711.
31. WILSON, J.B., TURNER, W.R., and SALE, J.W. 1927. Studies on bottled cocoa beverages. II. Efficiency of hydrogen peroxide in preserving cocoa-milk beverages. *Am. Food J.*, 22, 347-348.
32. YOSHPE-PURER, Y., and EYLAN, E. 1968. Disinfection of water by hydrogen peroxide. *Health Lab. Sci.*, 5, 233-238.
33. ALEXANDER McKILLOP and JOHNATHAN A. FARBIN, "Sodium Perborate-A Cheap and Effective Reagent for the Oxidation of Anilines and Sulphides," *Tetrahedron Letters* 24(14):1505-1508 (1983).
34. JOHN KIWI, "Oxygen Evolution Mediated by RuO<sub>2</sub> Colloidal Redox Catalysts in Aqueous Systems," *Journal of the Chemical Society, Faraday Transactions II*, 78, 339-345 (1982).
35. R. MAGNE, J.R. BERTHELIN, and Y. DOMMERGUIS. 1974. Solubilization et insolubilization de l'uranium des granites par des bacteries heterotrophes. In *Formation of Uranium Ore Deposits*. International Atomic Energy Agency. Vienna, pp. 73-88.
36. HENRY LUTZ EHRlich, 1981 In *Geomicrobiology*. Marcel Dekker, Inc. New York. Basel. pp. 297-298.
37. JAMES E. ZAJEC. 1969. Uranium Biogeochemistry. In *Microbial Biogeochemistry*. Academic Press. New York and London. pp. 179-194.
38. YOSHISO OGATA and HIDEO SHIMIZU, "Oxidation of Organic Compounds with Perborates or H<sub>2</sub>O<sub>2</sub>-Boric Acids," *Bulletin of the Chemical Society of Japan*, 52(2):635-636 (1979).
39. CHUANFAN QIAN, PAUL F. SANDERS, AND JAMES N. SEIBER, "Accelerated Degradation of Organophosphorus Pesticide with Sodium Perborate," *Bulletin of Environmental Contamination Toxicology*, 35(5) 682-688 (November 1985)
40. KENNETH J. HOFSTETTER AND BEVERLY S. AUSMUS, "The Identification and Control of Microorganisms at Three Mile Island Unit 2," *Nuclear technology* 87:837 - 844 (December 1989)
41. BEVERLY S. AUSMUS, V.A. BASTON, LAURA A. HOFMAN AND KENNETH J. HOFSTETTER, "Water Quality in TMI-2: Characterization of the RCS and Water Systems Supporting Defueling and Decontamination," TMI-2 Project Report (September 1986)
42. V.F. BASTON, K.J. HOFSTETTER AND R.F. RYAN, "A Comparison of Measured Radionuclide Release Rates from Three Mile Island Unit-2 Core Debris for Different Oxygen Chemical Potentials," *Nuclear Technology* 76:377-(1987)
43. ANTHONY H. ROSE, "Chemical Microbiology," Butterworths & Co, 247 pages (1965)
44. MASAYORI INOUYE (Editor), "Bacterial Outer Membranes As Model Systems," John Wiley & Sons, Inc, 449 pages (1987)
45. K. AKAMINE, K.J. HOSFTETTER, AND V.F. BASTON, "Characterization of Suspended Particles in Three Mile Island Unit-2 Reactor Coolant Water," *Nuclear Technology* 84:152-156 (1989).
46. D.N. POPE, "A Study of Microbiologically Influenced Corrosion in Nuclear Power Plants and a Practical Guide for Countermeasures," NP-4582, Electrical Power Research Institute (May 1986).
47. S.E. SHUMATE, C.W. HANCHER, G.W. STRANDBERG, and C.D. SCOTT. 1978. Biological processes for environmental control of effluent streams in the nuclear fuel cycle. p. 347-355. In R.G. Post and M.E. Wacks (ed) *Proceedings of Waste Management and Fuel Cycles '78'*. Univ. of Ariz. Press, Tucson.
48. J.E. ZAJEC and Y.S. CHIU. 1972. Recovery of heavy metals by microbes. *Dev. Ind. Microbiol.* 13:91-100.
49. P.R. NORRIS and D.P. KELLY. 1979. Accumulation of metals by bacteria and yeasts. *Dev. Ind. Microbiol.* 20:299-308.
50. W.A. CORPE. 1975. Metal-binding properties of surface materials from marine bacteria. *Dev. Ind. Microbiol.* 16:249-255.
51. P.R. DUGAN and H.M. PICKRUM. 1972. Removal of mineral ions from solution by microbiololy produced polymers. *Purdue Univ. Eng. Ext. Ser. Eng. Bull.* 141:1019-1038.
52. S.B. SAVIN. 1961. Analytical use of arsenazo III: determination of thorium, zirconium, uranium, and rare earth elements. *Talanta* 8:673-685.