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Long-term immersion of acrylic in biocides.

SNO-STR-97-024. B. Knox. 25th August 1997.

Introduction.

With any water system, even an ultra-pure water system, there is the possibility of bio-fouling occurring. There is normally no real alternative to treating this by the use of biocides. This can be done on a regular basis as a preventative measure or by waiting until fouling is detected and then applying treatment. However in the case of SNO there are parts of the system which could be adversely affected by use of some biocides and prior testing is necessary.

There is literature available on this subject and specialist journals exist. A useful review of the types of biocides available and their recommended dosing levels is given by M.W. Mittelman, pp.30-40 and 70, Microcontamination, January 1986. See also SNO-STR-91-072.

There are two main types of biocide. One is the oxidising type, the most commonly used being chlorine. Others which find use are ozone, chlorine dioxide, peroxides, iodine, etc. Then there are a variety of non-oxidising biocides which work in a variety of ways:
quaternary ammonium compounds,
formaldehyde, glutaraldehyde, etc,
anionic and non-ionic surface-active agents,
ethanol-derived or based on other alcohols,
phenolic and similar compounds,
strongly alkaline solutions, etc, etc.

In the particular case of pure-water systems, where nutrient levels are low, biofouling is almost entirely present as biofilms on surfaces. Free-swimming bacteria are few. The structure of these biofilms is being actively studied using new techniques. See for example the article "Slime City", New Scientist, pp.32-36, 31 August 1996. There are two important points to be made. One is that bacteria living in biofilms

are quite well protected and adequate concentration of biocide must be used to ensure a complete kill. The other is that killing the bacteria is not sufficient, since the dead organisms will remain adherent and form a source of nutrients for the biofilm to re-grow. The dead biofilm must therefore also be loosened and washed off. A blend of biocides and detergents may be used, or a multi-stage treatment may be preferred. Finally the chemicals used must be flushed out with clean water before the system is put back into use.

Initial concern was focused on the AV since it is essential that no chemicals which are likely to attack the AV are used. But other parts of the SNO detector and its water system must also be considered. For example the coated aluminium petals of the concentrators may be attacked by some biocides.

It was expected that the concentration of biocide used might be a significant factor, but that at the concentrations normally used acrylic should have good resistance to biocides. The effect of phenolic compounds has been investigated by immersing samples of PMMA in phenol solutions of various concentrations and it was shown that concentrations higher than 0.1% should be avoided. See SNO-STR-97-001. But the effect on acrylic of prolonged contact with low concentrations of biocides was also of some concern.

2. Acrylic samples for long-term tests.

At the time these tests were started samples of the acrylic sheet to be used for SNO were not available. The only acrylic sample of suitable material with identifying marking readily available was a small sheet of acrylic about 8 mm thick which had protective paper attached bearing the legend: ROHM & HAAS, PHILADELPHIA, OROGLAS, ACRYLIC PLASTIC. This was cut into samples measuring about 120 mm by 30 mm and the protective paper removed by soaking in detergent solution followed by rubbing off with a cloth and then washing with tap water followed by deionised water.

In September 1991 these samples were placed in glass bottles filled with solutions of various types of biocides that might be used. Some of the samples were inspected in December 1991 but no effect on the acrylic could be detected by visual examination. The samples were therefore left immersed until recently, a period of nearly six years. The storage temperature was about 22 C.

In August 1997 the samples were taken out, rinsed by being immersed briefly in a beaker of UPW, dried by contact with absorbent paper, and then examined.

3. Results of long-term immersion tests.

Sample no. 11. Immersed in "Domestos" household bleach, diluted 1:100, from 9-9-1991 until 1-8-1997. No obvious effects.

Sample no. 16. Immersed in "Adesol 20" biocide, diluted 1:100, from 9-9-1991 until 1-8-1997. No obvious effects.

Sample no. 26. Immersed in "Adesol 20" biocide, diluted 1:250, from 9-9-1991

until 1-8-1997. Was not fully immersed. May be some slight deposit.

Sample no. 27. Immersed in Formalin solution, phosphate-buffered, pH 7.2 to 1 (BDH - Gurr), used as received, from 9-9-1991 until 1-8-1997. No obvious effects.

Sample no. 30. Immersed in sodium hypochlorite solution, GPR, diluted 1:1000, from 9-9-1991 until 1-8-1997. No obvious effects.

Sample no. 33. Immersed in glutaraldehyde solution, 5% (50% solution diluted 1:10), from 14-9-1991 until 1-8-1991. Very slight deposit.

Sample no. 35. Immersed in hydrogen peroxide solution, 3% (30% solution diluted 1:10) from 14-9-1991 until 1-8-1997. No obvious effects.

Sample no. 38. Immersed in sodium hypochlorite solution, GPR, diluted 1:140 (about 0.1% Cl) from 18-9-1991 until 1-8-1997. Surface was wetted but no other obvious effects.

Sample no. 40. Immersed in sodium hypochlorite solution, GPR, diluted 1:1400 (about 0.01% Cl) from 18-9-1991 until 1-8-1997. Surface slightly wetted but no other obvious effects.

Sample no. 41. Immersed in UPW from a Milli-Q system (Millipore) as a control sample from 18-9-1991 until 1-8-1997. No obvious effects.

Sample no. 45. Immersed in "Kleeneze" quaternary disinfectant, 1% solution, from 4-11-1991 until 1-8-1997. No obvious effects.

Sample no. 46. Immersed in Gerrard A.S.A.B solution, 0.2%, from 4-11-1991 until 1-8-1997. No obvious effects.

Sample no. 47. Immersed in Gerrard A.S.A.B solution, 1%, from 4-11-1991 until 1-9-1997. No obvious effects.

4. Information on the biocides used.

The "Domestos" Thick Bleach is a household bleach which was held as a stores item. It claims to contain between 5% and 15% sodium hypochlorite and less than 5% non-ionic surfactants. Recommended dilution depends on the material being disinfected and the contact time. From 1:1000 up to 1:130 are suggested.

"Adesol 20" is a commercial biocide, at that time supplied by BDH but now sold by Coalite Fuels & Chemicals Ltd., Buttermilk Lane, Bolsover, Derbyshire, England. Tel. 01246 822281. Chemically it is dioctyl dimethyl ammonium chloride, and thus is one of the quaternary ammonium compounds. Recommended dilution for pure water systems was about 1:4000, but there was little experience to base this on.

Formalin solution, phosphate-buffered, (BDH - Gurr) pH 7.2-7.4, was sold as a histological fixative but could also be used as a biocide. A slightly different solution is now sold, as are similar solutions.

Sodium hypochlorite solution, GPR, BDH. This is a standard reagent containing about 14% available chlorine, and widely used as a bleach and biocide. Recommended dilution to about 50-100 ppm of chlorine.

Glutaraldehyde solution, 50%, GPR, BDH. This is a less toxic alternative to formaldehyde. Normally used diluted by at least 10 times.

Hydrogen peroxide solution, GPR, 100 volumes (about 30%), BDH. A commonly-used oxidising biocide particularly when the use of chlorine is undesirable. Quite strong solutions, up to 10% or more, are suggested. It is claimed that some bacteria can develop considerable resistance to hydrogen peroxide.

"Kleeneze" quaternary disinfectant is a commercial product based on quaternary ammonium compounds with surfactants and other agents added. Similar products are widely available, and a dilution to 0.5% or 1% is normally recommended for most purposes.

Gerrard A.S.A.B is a concentrated non-corrosive broad-spectrum bactericide and fungicide, effective against most bacteria, yeasts, moulds and spores. Supplied by Fisher Scientific. A dilution to about 0.2% or 0.5% is recommended for most applications.

5. Conclusions.

Although only visual examination has been used, the evidence so far is that "Oroglas" acrylic has good resistance to even long-term contact with a wide range of biocides and cleaning agents when these are used at dilutions similar to those recommended by the suppliers. The acrylic used for fabricating the AV is expected to have very similar resistance.

The samples used in these tests will be retained and can be made available for any further tests if desired.