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**ACTIVITY BUILDUP-UP
CONTROL BY HIGH pH COOLANT -
A LITERATURE SURVEY**

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ABSTRACT

A survey was made of unclassified literature dealing with the control of activity buildup in pressurized water reactors by high pH coolants. The survey concludes that a high pH coolant is desirable for control of induced radioactivity buildup in pressurized water reactors containing significant amounts of stainless steel, and no significant hazards are introduced by adoption of a high pH coolant. Lithium hydroxide was found the most acceptable means of coolant pH control. Strong base form mixed bed resin is effective in maintaining both coolant pH and coolant purity.

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1.0 INTRODUCTION

The coolant in light water moderated nuclear power plants functions both as a coolant and as a moderator. The coolant also is involved in several secondary processes which affect reactor operation. Coolant chemistry is designed to minimize the deleterious aspects of these side processes, which are:

1. Corrosion of reactor mechanisms and structural elements exposed to the coolant.
2. Transport and deposition of corrosion products.
3. Nuclear reactions of coolant and impurities and transport of activated materials.
4. Radiation-induced chemical reactions, both dissociation and synthesis, of coolant and impurities.
5. Transportation of fission products in the event of fuel element failure.

It is axiomatic that design is limited by the state of the art in any area of technology. Reactor coolant chemistry is a new field; its very newness creates a need to re-evaluate the technology periodically to take advantage of improvements which may be developed. This literature survey was made to provide a firm basis for consideration of high pH coolant recommendations for Army reactors. Work was performed under Item 5.1 of Task 5, PWR Support and Development Program.

In Army reactors, control of the secondary processes is by hydrogen addition and by purification of a coolant side stream. Hydrogen is added to minimize corrosion by inhibiting the dissociation reaction. ⁽¹⁾ Side stream purification of coolant is used to control the impurities and to reduce activity buildup by removal of induced and possible fission product activity. ⁽²⁾

Buildup of radioactivity on walls of primary systems has indicated that neutral water conditions do not allow effective control over the slowly migrating mass of radioactive corrosion products in the primary piping. ⁽³⁾, ⁽⁴⁾ More effective control has been observed in systems operating at a high pH (of 9.5 to 10.5). ⁽⁵⁾, ⁽³⁾ The improvement noted has resulted in the adoption of high pH coolant in a number of pressurized water systems including the large Shipingport P. W. R. power plant. ⁽⁶⁾ Hydroxides of lithium, potassium, sodium and ammonia have been used for the pH control.

The major factors upon which the selection of pH and pH control agents should be based are listed below.

1. System reliability shall not be compromised. (The change in pH shall not have any deleterious effects on cooling or moderating features of the coolant.)
2. System habitability shall be improved. (A reduction in coolant and deposit activity must result from changes induced in the secondary processes by the change in pH.)

2.0 SUMMARY OF THE LITERATURE

2.1 EFFECTS OF pH ON THE PRIMARY SYSTEM

The corrosion rates of the major materials of reactor construction (austenitic stainless steels) exposed to primary coolant are quite low at neutral pH (5 to 15 mg/dm²/mo). Experimental evidence is accumulating that corrosion of stainless steel systems operating at high pH becomes negligible after a relatively short time. (7) The statistical fluctuations in studies made to determine the effects of pH mask the reduction in corrosion and a specific evaluation of the reduction has not been possible. Theoretical studies (8) on metals which evolve hydrogen directly (such as stainless steel) show that there is an upper limiting pH. Above this pH, corrosion is not pH sensitive; below it, increasing corrosion may be expected as the pH is lowered.

Inhibition of both pitting in crevices and "deep" attack of austenitic stainless steel has been noted when the pH is increased to 10 or 11. (9), (10) Oxygen must be kept low because of the increased attack on ss with chromate formation at high pH. (1) Oxygen is normally excluded from reactors operating at neutral pH, so the problem is not of real significance.

The minor structural materials used in the SM-1 primary system (i. e., graphitar, type 410 ss and K Monel) show either a decreased corrosion, or are relatively unaffected as the coolant pH is increased to 10. (11) One exception to this statement is Stellite 3, which may have a slightly increased susceptibility to corrosion. The increase is not significant, because the stellites are used in moving parts and mechanisms and it has been found that high pH does not reduce operability of such mechanisms. (5)

In high pH systems, the possibility of caustic stress corrosion may be a problem if crevices or other areas exist in which concentration by boiling may occur. Lithium hydroxide appears to be less aggressive than either potassium or sodium in caustic embrittlement and cracking of austenitic stainless steel under local boiling conditions. (12), (13) This may be due to the limited solubility of lithium hydroxide. (12)

The effect of high pH on the effectiveness of decontaminating solutions is not clearly defined. Some reduction in effectiveness of alkaline permanganate citrate decontamination of systems operated at elevated pH has been noted at KAPL. (13) This may be a result of the increased tenacity of the crud deposits.

In summary, corrosion does not affect system integrity at neutral or high pH, and is probably reduced with high pH coolant. Operation of mechanisms is also not affected. Bettis studies on pressurizer heaters have indicated that caustic stress corrosion is not a problem with lithium hydroxide pH control.

Corrosion products (crud) form a more tenacious film in high pH coolant. (6) Studies with ammonia show a minimum pH of 10 is required for crud control. (14) At the higher pH, the yield of transportable crud is greatly reduced (1) and the deposition of crud is inhibited. (2) On the other hand, Van de Graff studies (15) have shown that under irradiation there is no significant deposition difference between pH 7 and pH 10 on type 304 ss. Crud levels in the coolant are reduced by a factor of about 100 at the higher pH (5) and the colloidal crud is more filterable. (15)

It may be concluded that transport of radioactive crud is reduced because of the more tenacious crud films. With less transport and inhibited deposition, buildup of radioactivity on out-of-core surfaces will be reduced at high pH. The efficiency of heat transfer in the core should not be affected by change in pH since radiation does not significantly alter deposition on stainless steel.

2.2 SELECTION OF pH CONTROL AGENT

A pH of at least 10 is required for crud control. (14) The lowest pH compatible with crud control should be used in order to keep the required amount of pH control agent at a minimum. The bases which may be used for pH control are ammonia, lithium, potassium or sodium.

Ammonia does not give any induced radioactivity, but it does undergo radiolytic dissociation. (14) To prevent dissociation, relatively large quantities of nitrogen and hydrogen must be dissolved in the coolant. The possibility of pump cavitation resulting from the dissolved gasses makes ammonia an unattractive pH control agent.

Sodium or potassium, if used for pH control, would create a radiation problem. High strength gamma radiation results from the induced nuclides of Na^{24} and K^{42} . Although it appears this would not be a problem in the SM-1, a hazard might develop when higher flux reactors, such as the SM-1A, are put into operation.

A possible hazard in the use of lithium arises from tritium produced by an (n,α) reaction on Li^6 . Calculations have shown that no tritium hazard will result from the use of natural lithium in the SM-1. (16) Should a hazard be indicated in higher power future reactors, the tritium hazard may be obviated by the use of Li^7 . The technology developed with natural lithium would be applicable with no loss in value.

The use of lithium for pH control is commended by several other effects. Lithium hydroxide does not increase the radiolytic decomposition of the coolant. (2) A great deal of experience in the use of LiOH has been gained at various pressurized water reactor installations, and no significant drawbacks were noted. The use of LiOH has been shown to produce all the advantages to be

expected at elevated pH. As noted earlier, lithium hydroxide is less aggressive than other group I hydroxides in initiating caustic stress corrosion. Base form resin can maintain more effective pH control with LiOH systems than with potassium or ammonia systems. (3)

2.3 USE OF EXCHANGE RESINS TO MAINTAIN COOLANT PURITY AND CONTROL pH IN HIGH pH SYSTEMS

Reference (3) contains an excellent discussion on behavior of base form resin, substantiated by numerous tests, including in-pile loop and reactor operations. The main conclusions are summarized below.

The resin is used as a mixed bed made up of two parts by volume of Amberlite IRA-400 in the hydroxyl form and one part Amberlite IR-120 in the cation form (equivalent resins may be substituted). The resin is able to maintain good control of pH if the ratio of primary surface to makeup is 5900 to 8800 ft²/gph. Initial addition of chemicals is required, as is make-up when the system is partially drained.

The ability of the resin to control crud is unimportant because the high pH itself provides the required control, but the resin must control ionized and colloidal impurities (including radioactive ones) in the coolant.

With a strong base form cation resin the rate of elution of monovalent cations is high and depends upon the equilibrium constants. There is a temporary hold-up in the resin which allows decay of most ionized radioactive products. The result is an effective decontamination in spite of the high leakage rate. Cs¹³⁷, a long-lived fission product, is a notable exception. The resin does tend to maintain Cs¹³⁷ constant and at a lower level (by the "fly-wheel" effect) than does a system with no purification. Calculations⁽¹⁶⁾ for the SM-1 show Cs¹³⁷ would be no problem at cladding escape rates compatible with reactor operation even if no hold-up in the resin existed.

Halogens, including radioisotopes, are removed effectively, as are divalent cations with half-lives of at least 50 days (Sr and Ba).

Colloidal isotopes are not effectively removed nor are colloidal daughters retained in the resin bed. Such elements as Zr, Ni, Y, Ru, Rh, and rare earths are classed as colloidal. This is not significant or disturbing, however, since in basic reactor coolant, colloidal isotopes are absorbed on the walls of the system and are not released to the purification system.

In summation, strong base form mixed-bed resin functions effectively in the dual role of maintaining coolant purity and pH. One exception to this rule occurs if air in-leakage produces significant ammonia concentrations in the coolant. The lithium in the resin is displaced by the ammonia, causing the coolant pH to rise. This, again, is not a significant drawback because care is normally taken to exclude air from systems operated at neutral pH.

3.0 CONCLUSIONS

- A. High pH coolant is desirable for control of induced radioactivity in pressurized water reactors with stainless steel present in significant amounts.
- B. No significant hazards are introduced by the use of high pH coolant either with respect to plant integrity or operability.
- C. Lithium hydroxide is the best choice for controlling the pH of the coolant.
- D. Strong base form mixed-bed resin functions effectively in the dual role of maintaining coolant purity and pH.

4.0 BIBLIOGRAPHY

1. Rockwell, T., and Cohen, P., "Pressurized Water Reactor (PWR) Water Chemistry," Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, V. 9, p. 536, United Nations, New York, 1956.
2. Medin, A. L., "Literature Survey for Activity Build-Up on Reactor Primary System Components," APAE No. 25, January, 1958.
3. Simons, G. P., et al, "The Performance of Base Form Ion Exchangers for pH Control and Removal of Radioisotopes from a Pressurized Water Reactor System," WAPD-TM-215, July, 1960.
4. Brown, W. S., et al, "SM-1 Research and Development Activity Build-Up Program, Task I Final Report," APAE No. 51, June, 1959.
5. Cohen, P., "Shippingport Coolant Technology," Bettis Technical Review, WAPD-BT-12, 1959.
6. Lindsay, W. T., Jr., "Safeguards Aspects of PWR Reactor Coolant Chemistry," WAPD-SC-546, 1957.
7. TID-8502, "Advanced Pressurized Water Reactor Study, Phase I Report," Part I, Stone and Webster Engineering Co. and Combustion Engineering Co., July, 1959.
8. Bockris, J., "Modern Aspects of Electrochemistry," Academic Press, New York, 1959.
9. Vlanovski, I. B., and Karwin, Y. M., "Crevice Corrosion of Stainless Steel," Zhur. Fiz. Khim. :33, p. 148, 1959.
10. Vaughn, L. H., and Ferguson, K. M., "Corrosion of Various Materials in High Temperature Water," BW-5250, June, 1957.
11. Depaul, D. J. ed., "Corrosion and Wear Handbook," TID-7006, March, 1957.
12. Stephan, E. F., and Miller, P. D., "Solubility of Lithium Hydroxide in Water and Vapor Pressure of Solutions of Lithium Hydroxide Above 220°F," BMI-1329, March, 1959.

13. Schultz, B. G. , Personal Communication to C. R. Bergen, Alco Products, Inc. , November 16, 1960.
14. Cohen, P. , "Ammonia Synthesis Test," WAPD-CP-535, 1954.
15. Thomas, C. C. , and Læcockm, H. W. , "Corrosion Product Transport and Deposition Under Ionizing Radiation," YAEC-93, 1958.
16. Cox, J. F. , Personal Communication to C. R. Bergen, Alco Products, Inc. , December 2, 1960.
17. Hasse, R. A. , "Effectiveness of the SM-1 Demineralizer for Reducing the Activity of Radioactive Liquid Wastes, Final Report - Test 205," Alco Products, Inc. , January 11, 1960.
18. WAPD-BT-16, "Reactor Chemistry and Plant Materials," December, 1959.
19. Hasse, R. A. , "Activity Survey in the Primary System and Make-Up Tank," Alco Products, Inc. , June, 1960.
20. Pement, F. W. , "Caustic Induced Stress Cracking in Stainless Steel," WAPD-BT-16, 1959.
21. Demmitt, T. F. , "Preliminary Report on pH Control by Ion Exchange in High pH Systems," HW-64403, 1960.
22. Thomason, P. F. , "Spectrophotometric Determination of Lithium," Analytical Chemistry, 2810, p. 15-27, 1956.