I have examined with real interest your proposal titled as above and submitted as MSR 70-58 to M. W. Rosenthal on August 26, 1970.

I see no a priori reasons why alkali chloroaluminates or mixtures thereof should be excluded as secondary coolants for MSBR's. The freezing points are very low—so the startup problem should be greatly eased, the viscosity seems first rate, and the thermal conductivity and specific heat should prove acceptable. I am inclined to agree that corrosion at and below 650 °C can be shown to be acceptably low and with a good chance that mass transfer with Hastelloy N will be satisfactory.

The situations at the steam and the fuel interfaces are somewhat less ideal. There might be real corrosion troubles (perhaps even stress corrosion cracking) in the event of a steam leak, but the situation may not be markedly worse than with NaBF₄ mixtures. Small leaks into the fuel should not prove intolerable since (1) no energetic reactions would ensue, (2) chloride should be removable by HF treatment, (3) aluminum, which will not be removed by Bi extraction schemes (Al and Bi form "immiscible" liquids), has a relatively low cross section, and (4) sodium from NaAlCl₄ is no worse than that from NaBF₄. Moderate leaks might result in insoluble fluoaluminates; that can be tested in due course and even if it occurs it should not in itself kill the notion.

Incorporation of hydrogeneous compounds into such melts (or any other suitable coolant melts) to provide a sink for the tritium produced by nuclear reactions in the fuel is a most desirable goal; an adequate solution to the implied problem is so important to us that no real possibility should be overlooked. The several mixtures which you describe in your proposal under Class I would be excellent for the purpose if they will work. I am, however, less optimistic than you seem to be about their chances for success. My pessimism has its basis in the lack of high temperature stability for the species you suggest.

Ammonia is, of course, thermodynamically unstable even at relatively low temperatures. For example, the reaction

\[ \text{NH}_3 \rightarrow \frac{1}{4} \text{N}_2 + \frac{3}{2} \text{H}_2 \]
comes to equilibrium—even at a total pressure of 30 atmospheres—at about 68 volume % NH₃ at 200°C and at about 1.5 volume % NH₃ at 600°C. This fact would seem to rule out NH₄⁺, since—if we are to hold up 99+% of the tritium—we would require that the "sink" compound be quite stable toward decomposition.

On the other hand, the reaction shown above is extremely sluggish; as you know, the synthesis of ammonia is done at high temperatures (550-600°C) even though the equilibrium is much less favorable, and very sophisticated catalysts are employed to get a rapid approach to equilibrium even at these temperatures.

The homogeneous decomposition is, of course, imperceptibly slow at reasonable temperatures. NH₄Cl, for example, can be distilled at about 330°C. [It is probably more accurate to say that it is decomposed into NH₃ + HCl at that temperature and recombined without sensible loss at condenser temperature.] It is, therefore, possible that one might use low concentrations of NH₄⁺ at 625°C if the system is uncatalyzed. I am much afraid, however, that the system will be "catalyzed"; the very large gamma dosage in the primary heat exchanger will, I expect, serve as a reasonable catalyst, and we will experience more decomposition than we can stand. [From considerations such as these I have, accordingly, dismissed without test the notion that NH₄F could be usefully incorporated into the NaF-BF₃ system now proposed as the coolant. NH₃ removal and recovery from that system would be complicated by the presence of BF₃ in the gas stream, but that difficulty should not of itself prove fatal.] But I must admit that some of the considerations above are fears rather than facts, and I may have been wrong enough to allow some margin of feasibility for the use of NH₄⁺ as a tritium scavenger. I hope so.

If we are to achieve the goal of releasing less than 1% of the tritium to the heat exchanger (and if we make the somewhat pessimistic assumption that the chemical sink in the secondary coolant must shoulder the entire burden) then the hydrogenous compound in the coolant (1) must have a great excess of H over T, (2) must exchange H for T readily, and (3) must undergo less than 1% decomposition (to produce free HT) during its residence time in the coolant. Since the production rate for tritium is about 0.1 equivalent per day requirement (1) above is readily satisfied; to supply combined hydrogen at 1,000 times the tritium production rate requires addition of (and withdrawal of) about 0.5 liter (STP) of NH₃ gas/minute. Requirements (2) and (3) seem—to some extent—mutually exclusive especially for a system that has no tendency to recombine once it is dissociated. Requirement (3) will obviously dictate the permissible residence time of NH₃ or NH₄⁺ in the coolant system. Simple arithmetic suggests that if that residence time is as short as 24 hours one is constrained to remove the 1 STP liter of NH₃ from about 40 gallons of coolant per minute; if we assume this addition and removal rate the NH₃ concentration in the coolant would be less than 1.5 ppm. If the dissociation is sufficiently slow to permit longer residence times
then one could make these additions to (and removals from) proportionately less coolant per minute and have a proportionately higher NH₃ or NH₄⁺ concentration in the coolant. [This treatment is grossly over-simplified but serves, I think, to give a ball park estimate of the problem.]

The key problem clearly seems to me to be the rate of decomposition of NH₄⁺ or NH₃ at high temperatures in the presence of the coolant salt, metal, and radiation. I suggest that the first experiments (after absorbing whatever information the literature has on NH₄⁺ and NH₃ decomposition) should be to ascertain whether the system (at NH₄⁺ concentrations in the 1,000 - 5 ppm range) is satisfactory as regards thermal decomposition to 650°C. If it is then we should look at the system in the radiation field of a HFIR fuel element which can give us the gamma dose level of the MSBR heat exchanger. If the system still looks feasible the rate of exchange of H for T should be investigated. If the system still lives after this there is still much to do but one could proceed with some hope and a bit of confidence.

It is my opinion that the alternative suggestions (pyridinium ion and quaternary ammonium and phosphorous compounds) for hydrogenous materials are less likely candidates than NH₄⁺ but (because of doubtful thermal stability) I again could be wrong.

I would, of course, very much like to have your help with this difficult and essential tritium problem. I feel sure that your proposal deserves a test; it seems to me to represent a big gamble for a big gain. It should be attempted—though I believe that the key go-no go issues should be examined as quickly as possible. I shall be glad to discuss any or all of the foregoing with you if you wish.

W. R. Grimes

WG:dc