Purity Control in Sodium-cooled Reactor Systems

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Recent advances in purity control in sodium systems are covered. Emphasis is placed on results from the prototype S.I.R. system as well as other unpublished data. Included are chemical and nuclear activation analyses of sodium, filtration data, and details and operation of cold traps and plugging indicators.

The development of sodium as a coolant for nuclear reactors has given rise to many interesting problems. One such area of interest is associated with purity control of the sodium. During the past months several (*1*, *2*) informative papers have been published on the subject. The present paper is an attempt to bring the reader up to date in the field of sodium-purity control. Emphasis is placed not only on previous unpublished work but also on experience gained in preliminary operation of the sodium-cooled submarine intermediate reactor (S.I.R.) project.

SODIUM SUPPLY

Sodium, available commercially from three American manufacturers: duPont, Ethyl Corp., and U. S. I. Chemical Corp., is produced electrolytically from salt and is extremely pure. A typical analysis of commercial sodium is given in Table 1. This assay represents an average of sixteen individual samples of sodium supplied by duPont for the S.I.R. Mark A power plant, a prototype of the power plant of the U.S.S. *Seawolf* (SSN575).

Because the Mark A plant was designed prior to widespread use of cast-drum sodium, its sodium charge was purchased in the form of 12½-lb. bricks. The principal impurities controlled in the purchase specification were calcium, to less than 400 p.p.m., and chlorine, to less than 50 p.p.m. Although not critical, these impurities were designated to assure a product consistent with that normally used in prior-development systems.

A special request was placed on the sodium supplier to provide sodium which was "cast dry," i.e., cast without the use of kerosene as a mold-release agent. In addition, it was requested that stop-cock valves not be heavily greased prior to running the Mark A order. This was done to assure absence of hydrocarbons. It is felt that the hydrocarbons in excess will decompose and carburize the stainless steel components of a sodium system (*3*). At Knolls Atomic Power Laboratory, carburized layers of approximately 1-mil thickness have been observed in tests up to 1,000°F. Although not excessively deep, such carburization is thought to weaken thin reactor parts which may be subjected to cyclic strains.

Because of a faint kerosenelike odor in sodium supplied to Mark A, careful analyses were made for hydrogen and carbon. Analysis of the molten metal indicated 50 and 100 p.p.m. respectively. The value of 100 p.p.m. carbon is felt to be well below that amount which would cause carburization. Analyses were performed by procedures outlined in references *4* and *5*.

As a remaining check on the impurity content in the Mark A sodium charge, samples were inserted for nuclear reactivity measurements in a thermal critical assembly. Results were in arbitrary units (cents of reactivity/g.) which, when converted, indicated that total parasitic absorption due to impurities was less than 18 p.p.m. boron or equivalent. As such, the nuclear poisoning effect of the impurities is less than 10% of the value calculated for pure sodium. Samples of Ethyl and U.S.I. sodium, tested in a similar manner, gave results identical to those from the duPont metal.

Substantiation of the purity of commercial sodium is available from recent radioactive decay data on Mark A sodium. After a period of 100-hr. operation the S.I.R. reactor was shut down and the sodium activity observed. The sample decayed for 13 days at the expected 15-hr. half-life. The impurity activity controlling after the thirteenth day leveled out at 27 days to a value 9 decades below the saturated Na^{24} level. Although this is a significant reduction in activity, it points up the need for complete system drainability of the sodium system. This is particularly true if maintenance is to be readily obtained on high-power-level reactor systems.

FILTRATION

Although the analysis of sodium indicates that the material is pure, it is advisable to filter the metal prior to introduction into a reactor system. Such filtration removes sodium oxide and also any insoluble foreign matter which may find its way into the commercial sodium.

In Mark A S.I.R. the brick sodium was melted in 900-lb. batches and forced through a filter into a transfer tank operating under vacuum. A second filter is located in this tank. The batches of sodium were transferred by positive pressure through this second filter to the system storage tank. The filters used in both tanks were sintered stainless steel with an average pore size of 5μ. Both

Table 1. Analysis* of S.I.R. Mark A Sodium

Element	P.p.m.	Method‡
Ag	< 1	S
Al	7.7	C
B	4	S
Ba	2	S
Be	< 1†	S
Bi	< 10†	S
Ca	191	C
Cd	< 1	S
Ce	2	S
Cl	30	C
Co	2	S
Cr	< 1	C
Cs	< 5	C
Cu	2	S
Fe	2.4	C
Hg	< 4†	S
In	< 2†	S
K	<100	C
Li	17	C
Mg	< 5	C
Mn	< 2	S
Mo	< 2†	S
Ni	0.5	C
P	< 10	C
Pb	1.1	C
Pd	< 5	S
S	14	C
Si	< 0.5	C
Sn	< 10†	S
Sr	5	S
Ti	< 10†	S
U	< 5	C
V	< 5	S

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*Sodium supplied by E. I. duPont de Nemours & Co. in 1954. Analysis of "as received" bricks performed by General Analytical Unit, Knolls Atomic Power Laboratory, L. P. Pepkowitz, Manager.

†None detected; value listed represents expected sensitivity of spectrographic detection.

‡S = spectrographic; C = wet chemical.

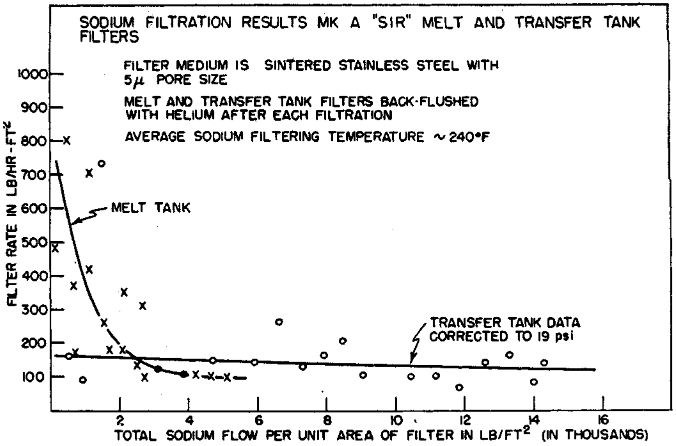

Fig. 1.

filters were back flushed with helium after each transfer.

As expected, heavy accumulations of sodium oxide occurred in the melt tank owing to the oxidized skin on the brick sodium. This necessitated the changing of filters and puddling and removing the oxide dross at approximately 6,000-lb. intervals. The filtration rate averaged 248 lb./(hr.)(sq. ft.) at an average temperature of 236°F. with a 19 lb./sq. in. differential.

The difficulties resulting from the excess dross on brick sodium points up the desirability of procuring sodium in rail car lots or in the cast in drum form. Even in using these forms, a filter is advisable. Filtration data taken on the Mark A transfer-tank filter would be applicable in these cases since the sodium filtered was relatively free of oxides. The average filter rate from the Mark A transfer tank was 177 lb./(hr.)(sq. ft.) at an average differential of 20.0 lb./sq. in. at 245°F.

Figure 1 plots data for the melt- and the transfer-tank filters. To allow comparison of the two operations, the transfer-tank-filter results were corrected. to a 19 lb./sq. in. differential by use of a ratio of pressures. There is no obvious explanation for the absence of high filtration rates during initial operation of this filter. It is expected that oxide deposition within the filter pores plays an important role in the results. The inconsistency in data may occur since the transfer-tank filter was original equipment and may have been exposed to sodium for a long period of time prior to use. On the other hand, data plotted on the melt-tank filter represent runs on the second and third filter replacements.

A chemical analysis after filtration indicated that of the impurities listed in Table 1 the only element which experienced a significant reduction was calcium. This decreased from 191 to less than 40 p.p.m. Calcium reduction results from its oxidation with the excess sodium oxide present in the brick melting tank.

CALCIUM IN SODIUM

If the sodium had been supplied in oxide-free tanks, such oxidation of calcium would not be expected to occur immediately upon charging. The possibility is therefore raised of admitting soluble, unoxidized calcium into a reactor coolant system. Subsequent oxidation would result in the formation of calcium oxide, which is insoluble and hence could cause hydraulic or mechanical difficulties.

The decrease of free calcium in sodium systems has been observed at Knolls for several years. The impurity tends to accumulate on the walls of the pipe and at low-velocity regions. In one experiment calcium was added to a flowing system equipped with a restricted-passage orifice plate. This plate, perforated with 50-mil-diam. holes, was intended to simulate the small flow passages in a power reactor. The loop was charged with sodium containing sufficient sodium oxide to cause sodium oxide plugging of the plate when the loop temperature was lowered to 525°F. On the addition of calcium to provide 500 p.p.m. calcium in sodium, the flow decreased to 84% of the original value. When enough calcium was added

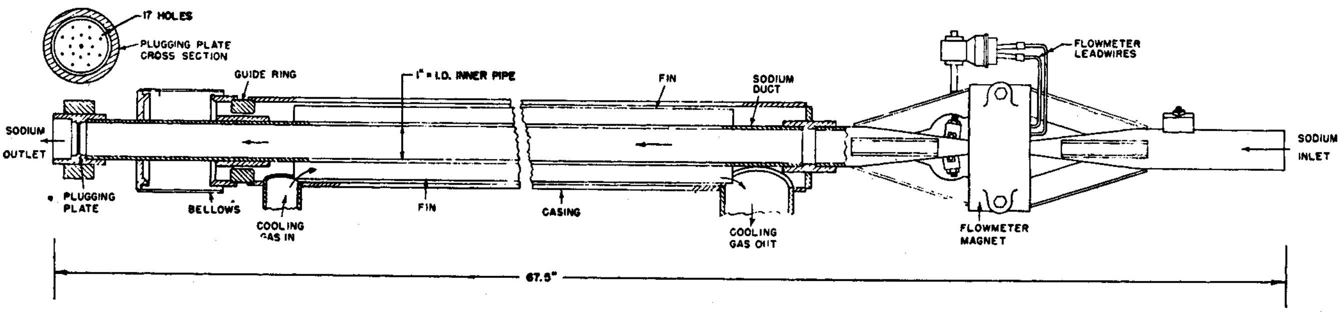

Fig. 2. Plugging indicator.

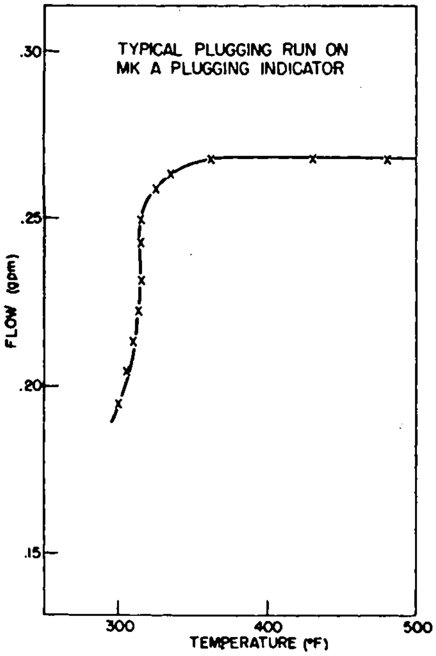

Fig. 3.

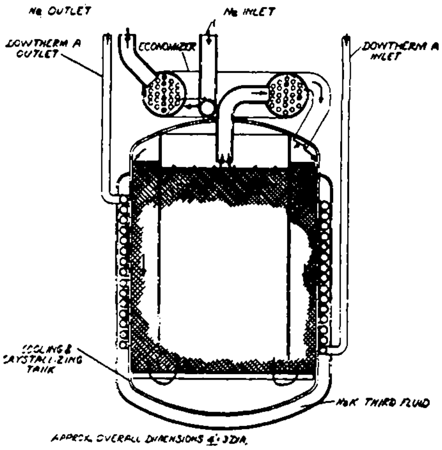

Fig. 4. Cold trap.

to raise the concentration to 675 p.p.m., flow decreased to 13% of normal. Subsequent dissection of the loop showed a calcium build-up of 1.5% at the perforated plate. Although solubility at loop temperatures is in excess of 1% calcium, a sample of the bulk sodium indicated only 2 p.p.m.

In view of the potential difficulties which may result from free calcium in sodium, caution should be exercised in the use of sodium which is received completely unoxidized.* Treatment by bubbling air through the molten fluid is one possible way of oxidizing, and thus removing, the calcium. An alternative is to purchase low-calcium sodium from the manufacturers. Although this is relatively new, as of this writing, two of the three sodium manufacturers can supply metal in tank-car lots with less than 50 p.p.m. calcium. The added cost for this product does not appear to be significant.

OXYGEN DETECTION

The principal impurity of concern in a sodium system is oxygen. The effect of the oxide on system pluggage, corrosion, and radioactive steel transport is discussed in the "Liquid Metals Handbook" (*1*). In order to monitor for oxygen in a sodium system, a plugging indicator can be used. Details of this instrument are discussed by Voorhees and Mausteller (*1*).

Figure 2 illustrates the plugging indicator used in Mark A S.I.R. Rated sodium flow is 0.3 gal./min. and the restricted passage consists of a thin plate with seventeen holes, each 0.046 in. in diameter.

Figure 3 shows a typical plugging run obtained by use of this unit. The break in the curve is distinct to within 35°F., resulting in accurate oxygen determination. With greater oxide concentrations, the knee in the curve would be even sharper. During the run shown, the plugging plate was cooling at a rate between 5° and 10°F./min.

The need for oxygen detection and control even after a system is carefully charged is illustrated by recent Mark A S.I.R. experience. The sodium was, as discussed above, double filtered at low temperature into the system storage tank. The storage tank and associated piping had been evacuated several times to a vacuum of 50μ. After each evacuation the system was repressurized to above atmospheric pressure with pure helium which had been further purified by passing through sodium potassium bubblers. The reactor-coolant system proper was also treated in a similar manner.

Despite the foregoing precautions, the oxygen content upon filling assayed at 0.019% O_2. It is probable that the total system oxide content was even higher, as only the oxide in solution can be detected. This excess above solubility was substantiated by a longer than usual cold-trapping time required to effect a reduction in the oxygen level.

Unfortunately, from a data standpoint, the initial operation was made with a sampler equipped for oxide determination by the conventional mercury-extraction technique (*6*). The device used was shielded evolution of the K.A.P.L. type II sampler (7). Somewhat later the system was fitted with a plugging indicator, thereby permitting very accurate oxygen control.

Recent data indicate that even after several months of operation, oxide is still building up at a rate of 7 g. of oxygen/day. Since no appreciable repairs have been undertaken and, further, since only a small fraction of this amount could be explained as oxygen from the inert gas, it is concluded that the oxygen is still being leached out as original impurities from the system. It must be stated, however, that "first time" caution has caused careful control of oxygen at levels (0.002% O_2) which are considered substantially lower than will ultimately be found necessary.

OXYGEN REMOVAL

The high degree of oxygen control in Mark A is readily maintained by use of a cold trap. The design of this unit is shown in Figure 4. It consists of a cooler-crystallizer section and a regenerative heat exchanger. Sodium, at a flow of 12 gal./min., is cooled in the regenerator from 600° to 750°F. The Dowtherm jacket in the crystallizer lowers the temperature an additional 70° to 300°F. This Dowtherm cooler assures that the lowest temperature exists in the crystallizer, thus providing for oxide accumulation in this region. In addition, the heat removed in the crystallizer provides the thermal driving force for operation of the regenerator. A more detailed description of the design features of this type of cold trap is found in reference *1*.

The crystallizer region of the Mark A cold trap is packed with a knitted stainless steel wire of 4 to 5 mils diam., packed to a density of 20 lb./cu. ft. This packing provides for the growth and support of the oxide crystals. The packing is a continuous strand of wire, considered necessary to prevent slivers of wire fiber from disengaging and causing mechanical difficulties in an otherwise clean reactor system. The volume of the crystallizer is approximately 80 gal. Aside from a capacity consideration, the volume provides approximately 5 to 6 min. holdup, which assures maximum efficiency in the crystallizer region.

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*Similar plugging difficulties may occur owing to formation of Mg^{24} from the decay of Na^{24}. Magnesium will oxidize in preference to sodium, forming insoluble magnesium oxide. For example, magnesium build-up in a sodium system which has a saturated activity of 1 curie/g. will be 46 p.p.m./yr.

The crystallizer size of the mark A cold trap was based on some unpublished studies conducted by B. G. Voorhees and the author on a small ½-in. piping loop equipped with a test cold trap. The cold-trap crystallizer was 4 in. in diam. and 20 in. long and was packed with stainless steel wool. The loop was equipped with a perforated plate which served as a plugging indicator.

Residence time in the crystallizer was varied by varying the sodium flow rate. The results are plotted in Figure 5 as oxygen concentration in the loop as a function of number of times the system volume was passed through the cold trap. The flow volume passed through the unit is thus a measure of cold-trap efficiency. It is seen from Figure 5 that an appreciable gain in efficiency results from increasing crystallizer hold time from 2½ to 5 min. These data indicate that little is gained in efficiency when residence time is increased from 5 to 10 min.

A subsequent run was made on a comparable size of cold trap in which the steel-wool packing was removed. Although the unit was effective, the rate of removal was considerably less than the units which employ the steel-wool packing.

An estimate of the capacity used to design the Mark A cold trap was also determined by Voorhees and the author. Runs were conducted in a cold trap employing a 15-gal. steel-wool–packed crystallizer. Oxygen, added as Na_2O and Na_2O_2, was permitted to reach equilibrium with the test-system sodium before the cold trap was activated. The test was carried out until 35 wt. % Na_2O was accumulated in the crystallizer region. No increase in pressure drop was detected when the test system was secured for other reasons.

The Mark A cold trap is used on an intermittent basis in purifying the sodium charge. A typical operating run in purifying the S.I.R. sodium is shown in Figure 6. A comparison of these data was made with the theoretical reduction possible, based on ideal mixing in the system. This analysis* indicated that the cold-trap discharge was saturated at the lowest cold-trap temperature and hence was 100% effective.

In discussing cold traps, the author emphasizes that units of the Mark A type are designed for high efficiency and with considerable emphasis on total radioactive-shield weight. Cold traps for central-station nuclear plants can be less complex if allowed to be larger or of lower efficiency. For example, data above indicate that packing is not absolutely essential; likewise, the regenerative heat exchanger could be eliminated. A simple cold trap, particularly well suited to small test systems, is the natural-circulation type described in reference *1*.

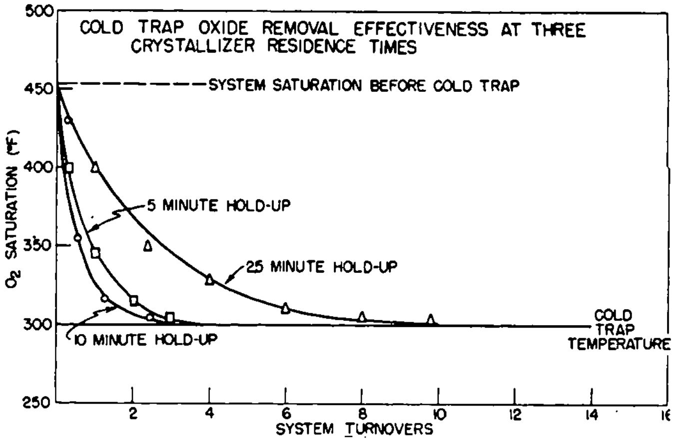

Fig. 5.

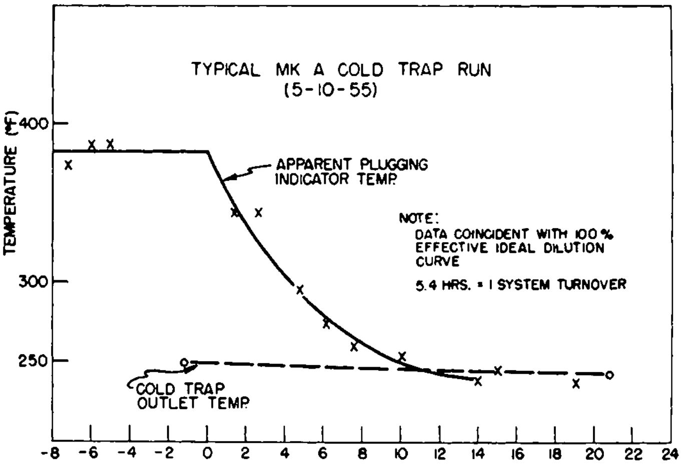

Fig. 6.

CONCLUSION

With time the technology of the use of sodium as a reactor coolant is becoming even more highly developed. It is significant that in the operation of the S.I.R. Mark A plant, purity-control considerations have worked out as anticipated. In general, this operation substantiates the author's belief that the purity considerations in using sodium are simple and no more complex than those involved in the use of other coolant fluids.

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LITERATURE CITED

1. Jackson, C. B., et al., Sodium-NaK Supplement, "Liquid Metals Handbook," 3d ed., U.S. Gov't Printing Office, Washington 25, D. C. (July, 1955).
2. Trocki, T., W. H. Bruggeman, and F. E. Crever, *Trans. First United Nations Sponsored Conference on Nuclear Energy* (August, 1955).
3. Brush, E. G., Knolls Atomic Power Laboratory, private communication.
4. Pepkowitz, L. P., and E. R. Proud, *Anal. Chem.*, 21, 1000 (1949).
5. Pepkowitz, L. P., Knolls Atomic Power Laboratory, private communication.
6. ———, and W. C. Judd, *Anal. Chem.*, 22, 1283 (1950).
7. Bruggeman, W. H., and G. Billuris, "Sampling of High Temperature Alkali Metals," Industrial Laboratories Publishing Company, Chicago (January, 1953).

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*The analysis was based on:

$$\frac{C - C_t}{C_s - C_t} = e^{-V_s}$$

where

C = instantaneous oxide concentration in the system
C_t = theoretical minimum oxide concentration at the cold-trap discharge
C_s = system oxide saturation at start of the cold-trap run
V_s = number of times the system volume was passed through the cold trap