SALT WASTE VOLUME REDUCTION
BY SODIUM REMOVAL

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September 15, 1973

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SUMMARY

A literature search and preliminary experiments were carried out to determine the feasibility of reducing salt waste volumes by the removal of sodium and purifying the sodium as metal for reuse or less restricted storage.

Included in the experimental part of the study were oxalate precipitation of sodium, preparation of chloride feed for electrolysis, denitration experiments, carbon reduction of sodium-cesium compounds and distillation of sodium metal for decontamination.

Each of these steps was found to be feasible but many problems exist. The most favorable process probably includes: evaporation and denitration (possibly preceded by a scavenging precipitation), reduction with carbon and distillation of sodium metal from the reaction mixture at low pressures, and purification of sodium metal by filtration and distillation. An alternative to the first step might be oxalate precipitation of the sodium.

Considerable development work remains before an integrated process could be demonstrated. Questions include materials of construction to withstand the severe corrosion during the calcination step and the reduction step. Methods of trapping the reduced sodium metal need to be devised. It was found that the nitrate level would have to be reduced to an undetermined low level (probably <10%) for a safe carbon reduction reaction. Thermal decomposition may have to be supplemented by chemical reduction to achieve this level. Excessive volatility of sodium and cesium compounds was observed during calcination.

SALT WASTE VOLUME REDUCTION

I. INTRODUCTION.

The simplest approach to the long term storage of Hanford's radioactive salt waste is to stabilize it and store it in place. It is also the lowest cost alternative.⁽¹⁾ In the event that this is judged inadequate, then transferral and processing of this liquid-solid slurry (commonly referred to as "salt cake") are necessary, and it becomes highly desirable to reduce the volume to minimize both transportation costs and the costs of future storage.

Calcining to remove water, convert nitrates to oxides, etc., will reduce the volume somewhat, but a major reduction in storage volume could be realized only if the sodium were removed as an inert byproduct. After decontamination, the sodium could be recycled to the economy in either a controlled or uncontrolled manner, or stored under less restrictive control, depending on its purity.

O. F. Hill⁽²⁾ outlined this approach and suggested that a study be initiated to evaluate sodium separation by electrolysis and purification by distillation. Discussions between personnel from ARHCO and BNW led to an increased scope of the study. Bartlett⁽³⁾ suggested that seven processes be evaluated, five of which involved sodium separation. A preliminary study was made in 1971 to better define the problem and to assess the feasibility of these processes. Included in this study were brief surveys of: 1) decontamination of salt cake solution by sodium oxalate precipitation, ion exchange and solvent extraction, and membrane separation; 2) conversion of sodium to metal by fused salt electrolysis or chemical reduction, sodium oxide production by calcination; and 3) decontamination of product by amalgam exchange, alcohol extraction of NaOH, sodium oxide distillation, and filtration and distillation of sodium metal. A review of this work is included in the present report.

Recommendations from the preliminary study were for additional work in the following areas: 1) further characterization of salt cake, 2) conversion of salt cake to sodium chloride, 3) calcination of the salt cake, 4) reduction to sodium using carbon, and 5) purification of sodium by distillation.

Laboratory experiments which were carried out in these areas are described below, and conclusions are presented along with recommendations for further work.

II. CHARACTERIZATION OF SALT WASTE.

A "typical" salt waste or salt cake solution is difficult to define. However, the composition of wastes in several tanks have been partially determined and other estimates of composition have been made. Table I shows data obtained by Schulz (ARHCO) for tanks 116-TX and 117-TX. ⁽⁴⁾ This may be considered representative of supernate from neutralized wastes. Larkin and Skolrud (ARHCO) ⁽⁵⁾ compiled composition ranges characteristic of feedstock for the in-tank evaporator. These data are shown in Table II. Table III is based on data from Hill's paper, ⁽²⁾ and the composition is similar to that used by Rey ⁽⁶⁾ and Schneider. ⁽⁷⁾ From Table III it may be noted that of the total solids, 70% by weight is sodium salts. Comparison of Tables II and III gives an estimate of the uncertainty or variability in tank composition. Iron, bismuth and small amounts of other elements are present as precipitates.

The other components of interest are the radionuclides. These will vary in concentration even more widely than the bulk chemicals listed above depending on the source of the waste (fuel source, age, etc.). Sheppard ⁽⁸⁾ reviewed the data available and made estimates of the principal fission products and actinides present in the waste. These are listed in Table IV. A 5-year cooling period was assumed.

TABLE I

SALT CAKE COMPOSITION

	<u>116-TX Tank-9/70</u>	<u>117-TX Tank-12/70</u>
	<u>Range</u>	<u>Range</u>
Percent Interstitial Mother Liquor (sampled from hard salt layers)	22 - 24	25
Moisture Content After Drying at 100°C, %	1 - 8	2 - 5
Moisture Content After Drying at 150°C, %	< 1	< 1
Salt Particle Density, g/ml	1.86	1.4 - 1.5
Radionuclides - Ci/Gal of Dry Salt (a)		
¹³⁷ Cs	.07 - .33	.13 - .21
⁹⁰ Sr	1.5×10^{-4} - 7.7×10^{-4}	2.5×10^{-5} - 5.4×10^{-4}
¹⁰⁶ RuRh	1.5×10^{-3} - 3.9×10^{-3}	2.5×10^{-3}
Cations, Major (Dry Salt Wt%) (b)		
Na	15 - 30	28
Fe	0.02 - .5	.07 - .2
Al	0.2 - .5	---
Si	< 0.05	.02 - .03
Water Leachability		
¹³⁷ Cs	90 - 98 percent	---
⁹⁰ Sr	3 - 5 percent	---
Thermal Conductivity BTU/hr-ft ² /°F	0.22 - 0.28	0.22 - 0.28

(a) The high Cs/Sr ratio results from Sr retention in the original tank solids.

(b) The remainder is made up of anions (see Table II).

TABLE II
PRELIMINARY ANALYSIS OF FEEDSTOCK

Na^+	7.0 - 9.5 <u>M</u>
AlO_2^-	0.2 - 1.7
OH^-	1.5 - 4.8 ^(a)
NO_3^-	1.5 - 4.3
NO_2^-	0.3 - 1.3
CO_3^{-2}	0.2 - 1.6
Cl^-	0.03 - 0.2
F^-	trace - 0.02
PO_4^{-3}	trace - 0.01
SO_4^{-2}	trace - 0.01
Fe^{+3}	trace - 0.01
SiO_3^{-2}	trace - 0.01
^{137}Cs	0.1 to 0.75 Ci/gal
SpG	1.35 - 1.45
pH	13.0 - 13.5
Viscosity	3.5 cp at 30°C ^(b)

(a) Terminal OH^- concentration in mother liquor may reach 15M to 18M after several evaporation cycles.

(b) Viscosity of terminal mother liquor may approach 22 cp at ~100°F.

TABLE III
TYPICAL SALT CAKE

	<u>kg in 2200</u> <u>Liters</u> (2)	<u>gm/per</u> <u>Liter</u>	<u>gm Sodium</u> <u>per Liter</u>	<u>M</u> (a)
Na_2SO_4	71	32	8.7	0.38
Na_2HPO_4	57	26	8.4	0.36
NaF	25	11	6.2	0.27
NaNO_3	1012	460	124	5.4
NaNO_2	807	367	122	5.4
NaOH	16	7.3	4.2	0.18
Na_2CO_3	212	96	41.7	0.90
NaAlO_2	410	186	52.3	2.27
Fe_2O_3	28	13	--	.081
Bi_2O_3	47	21	--	.028
H_2O	1787	812	--	45.1
Fission products and other activities				

(a) Molarity calculated on basis of all components dissolved.

TABLE IV
RADIONUCLIDE CONCENTRATIONS IN TYPICAL SALT WASTES (a)

Nuclide	($\mu\text{Ci/g Na}$)	($\mu\text{Ci/cc}$)
^{90}Sr	2.0×10^3	2.8×10^2
^{106}Ru	3.0×10^2	4.2×10^1
^{125}Sb	4.8×10^1	6.7×10^0
^{137}Cs	2.2×10^3	3.1×10^2
^{144}Ce	6.7×10^2	9.4×10^1
^{147}Pm	2.1×10^3	2.9×10^2
^{79}Se	1.0×10^{-2}	1.5×10^{-3}
^{93}Zr	7.4×10^{-2}	1.0×10^{-3}
^{99}Tc	3.6×10^{-1}	5.0×10^{-2}
^{107}Pd	8.2×10^{-4}	1.2×10^{-4}
^{129}I	6.4×10^{-4}	8.9×10^{-5}
^{135}Cs	6.9×10^{-3}	9.6×10^{-4}
^{151}Sm	3.0×10^{-1}	4.2×10^0
^{239}Pu (b)	3.5×10^{-1}	4.9×10^{-2}
^{238}Pu	1.1×10^0	1.5×10^{-1}
^{241}Am	2.3×10^{-1}	3.2×10^{-2}
^{242}Cm	3.5×10^{-3}	4.8×10^{-4}
^{244}Cm	3.1×10^{-1}	4.3×10^{-2}
^{63}Ni (c)	4.5×10^{-6}	6.3×10^{-7}
^{60}Fe (d)	$\sim 10^{-8}$	$\sim 10^{-9}$
^{60}Co (e)	5.5×10^0	7.7×10^{-2}
^{22}Na	Negligible	

(a) Five years after reactor discharge.

(b) Assumed 0.1 percent loss of Pu.

(c) Based on assumed 0.1 percent Ni in 2S Al slug cladding and 15 barn ^{62}Ni cross-section.

(d) Based on assumed 0.5 percent Fe in 2S Al slug cladding, 1.1 barn and assumed 0.1 barn cross-sections for ^{58}Fe and ^{59}Fe , respectively.

(e) Based on 6.4 $\mu\text{Ci/g Al}$, from HW-42612 (9)

Column two expresses the radioactivity in terms of a saturated sodium chloride solution. If one then uses MPC data from 10-CFR 20 or from the AEC Manual 0524 (Appendix), a decontamination factor to attain 10-CFR 20 could be stated for each nuclide. Sheppard indicates that these range from 10^9 for ^{90}Sr to 10 for ^{135}Cs . It is conceivable that the sodium could be reused in nuclear applications with much less stringent decontamination.

III. METHODS OF VOLUME REDUCTION.

The basic alternatives for treatment of salt wastes, aside from continued in-tank storage, are 1) bulk conversion to an insoluble form such as glass or basaltic material, and 2) separation of significant radionuclides and inert compounds. Schulz and Kupfer ⁽¹⁰⁾ have outlined possible approaches to the first alternative. These include high temperature processes, such as melting with basalt, the thermite reaction, and hydrothermal crystallization of insoluble silicates. The formation of glass-like products has been studied in considerable detail at all major AEC sites. At Hanford this was studied in detail in connection with the WSEP Program. ⁽¹¹⁾ It is quite likely that alternative (1) would be preceded by some separations of radioactive nuclides, e.g., the transuranics, or other long-lived radionuclides, or conceivably by the removal of the inert sodium. The latter is the only step that can offer a large volume reduction. Thus, sodium removal is a general concept that can have considerable impact on any method of salt waste disposal or storage.

IV. EVALUATION OF SODIUM REMOVAL METHODS AND EXPERIMENTAL WORK.

1. Precipitation Methods.

The precipitation of sodium oxalate from salt cake solution was briefly tested in the laboratory. This proposed step in the overall process for salt conversion of sodium into metal would permit a gross separation from the major fission products (^{90}Sr , ^{137}Cs) and conversion of the sodium salt to a common anion for further processing. The NaHC_2O_4 precipitate would be filtered or centrifuged and decomposed ($250\text{--}270^\circ\text{C}$) to the carbonate. The conceptual process is shown in Figure 1.

A simulated salt cake waste (Table III) solution was spiked with ^{22}Na , ^{137}Cs or ^{85}Sr tracer and titrated with oxalic acid. Figures 2 and 3 show the percent of each remaining in solution. The results indicate that the strontium initially precipitates as the carbonate (pH 10 to 3.5) and then goes completely back into solution with increasing acidity (pH <1). The cesium results appear questionable because, on initial addition of oxalate, ~16 percent of the cesium precipitated, and this was constant over a pH range of from 0.5 to 10. Washing the NaHC_2O_4 salt with 1M oxalate did not remove the cesium, and the contamination was confirmed on dissolution of the salt cake.

As shown in Figures 2 and 3 when the initial oxalate was added, 30-35 percent of the sodium precipitated above a pH of 8.5. At this point three moles of sodium precipitated per mole of oxalate added, indicating that other sodium salts e.g., Na_2CO_3 , may also initially precipitate. At a Na/oxalate mole ratio of 1, the amount of sodium precipitated appears to be a function of the volume of supernate. The solubility of sodium hydrogen oxalate is reported to be 3.7 $\text{NaHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ /100 of H_2O at 20°C or ~0.29M. For this experiment, using a 9M Na^+ feed and 1M oxalic acid, 70 percent of the sodium was precipitated at a Na/oxalate mole ratio of 1, and the final supernate was calculated to contain 0.29M Na^+ . To reduce this sodium loss, the oxalic acid concentration could be increased thus decreasing the supernate volume or the supernate waste could be sent to a concentrator for recycle.

Sodium hydrogen oxalate is a white, crystalline precipitate with a centrifuged density of 1.3 g/ml of precipitate; it filters readily on a coarse glass frit (40-60 microns). Thus, although cesium contamination of the precipitate is a problem and further studies would have to be made, the oxalate precipitation step is seen as a possible preliminary separation.

Other precipitants that have been considered include fluoride. The solubility of NaF is 40 g/l at 25° while the solubility of NaHF_2 is 37 g/l. At 100°C, NaF is unchanged while NaHF_2 becomes very soluble thus suggesting a possible purification cycle, as cesium fluorides are very soluble at both temperatures. Brief experiments indicated that excessive amounts of HF were required, and that the Cs separation was not promising.

FIGURE 1. PRECIPITATION OF SODIUM AS THE OXALATE

FIGURE 2. PERCENT Cs, Sr AND Na REMAINING IN SOLUTION,
pH ADJUSTED FROM 10.3 TO 0.65 WITH 1M AXALIC ACID

FIGURE 3. PERCENT Cs, Sr AND Na REMAINING IN SOLUTION AS A FUNCTION OF OXALIC ACID ADDED TO THE SYNTHETIC SALT SOLUTION

Precipitation reactions may be very useful in another sense, i.e. pre-precipitation of other constituents such as PO_4 , SO_4 , Fe, Al, etc. The scavenging effect may be very significant for nuclides such as Zr and Sr and for the transuranics, thus simplifying the sodium decontamination step. Addition of other cations to complete the removal of specific anions will enhance this decontamination. This was not studied in the present program.

2. Membrane Separation.

Ion selective membranes are appealing in that little processing is involved, thus leading to a simple, inexpensive operation. To be considered, any membrane process must have the following characteristics: high specificity for sodium in the presence of other metal cations; reasonably high diffusion rates; stability in a high radiation field; and reproducibility.

Most membrane technology has been in support of desalination of water by reverse osmosis. Some additional studies have been conducted on the treatment of secondary waste streams from sewage plants. However, the goal of all of these studies has been the production of "pure" water, not pure sodium salts.

After a preliminary literature search, it was concluded that there does not exist a membrane process applicable to the volume reduction of the Hanford Salt Cake Wastes. All presently known membranes would be extensively damaged by the radiation field, their behavior and activity toward the metal ions other than sodium have not been studied, and the reproducibility of membranes is not yet a reality.

3. Ion Exchange and Solvent Extraction.

There are two approaches to volume reduction by extraction; removal of the sodium or removal of a sufficient quantity of radioactive species that the waste can be considered subject to less stringent restrictions.

The use of cation exchange resins is not, a priori, a promising technique. The polyvalent ions are much more strongly absorbed than Group I ions. Also, normal cation resins show little selectivity among the monovalent ions. The fact that other metal cations will load on the resin with sodium

can possibly be overcome by selective elution of the sodium. This is a common technique and is currently being used at Hanford to enhance the separation of cesium from sodium using Duolite ARC-359 resin. Reichenberg⁽¹²⁾ points out that a reversed affinity sequence for the alkali metals is found with some carboxylate resins, resulting in the affinity decreasing in the order $\text{Li} > \text{Na} > \text{K} > \text{Cs}$. It is not likely that removal of sodium by ion exchange with adequate decontamination could be achieved. Radiolytic degradation of resins is also a problem. A secondary effect here is the increase in waste to be processed.

Solvent extraction has many of the same limitations since the polyvalent cations, which can form stable complexes are much more extractable into organic solvents than the Group I ions. Lithium, being a relatively small ion, can form a nitrate complex - or perhaps an ion pair - and extract fairly well into strongly basic solvents. Cesium, being a large ion can form unique ion pair complexes and extract in a number of ways. The polyiodide will extract into nitrobenzene⁽¹³⁾ with very high extraction coefficients. Dipicrylamine complexes will extract into nitrobenzene.⁽¹⁴⁾ Since the hydration energy of the large cesium ion is relatively small, many organic molecules, such as phenols, can compete with water and form a hydrophobic complex that will extract. Thus, BAMBP (4-sec-butyl-2-(α -methylbenzyl) phenol) was found by Brown and co-workers to produce preferential extraction of cesium.⁽¹⁵⁾ Bray⁽¹⁶⁾ extended the extraction studies to include a synergism effect.

The other alkali metal elements, Na, K and Rb, are generally very poorly extracted. Acid organo-phosphates will extract them in the order $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$,⁽¹⁵⁾ but under the same conditions most other metals are extracted one or more orders of magnitude better.

Cyclic polyethers have shown some sodium selectivity.⁽¹⁷⁾ The specificity is apparently a size effect.

If ion exchange or solvent extraction is to be used, a better approach to waste volume reduction would appear to be removal of other fission products away from the sodium. Considerable experience on the recovery of specific nuclides from waste, e.g., rare earths, cesium and strontium

is at hand. (18) (19) Separation of wastes into unique "packages" in this manner may turn out to be a feasible approach. The use of ion exchange may be limited by radiation degradation. However, both it and solvent extraction have the capability for such a separation. Clearly though, the preparation of decontaminated sodium by such a process or processes would be a monumental task and might well produce more waste than consumed.

4. Electrolytic Removal of Sodium.

The process envisioned by Hill⁽²⁾ consisted of removing insolubles, removing sulfates and phosphates by precipitation with calcium or barium, concentrating and drying, converting to chloride, and finally, electrolyzing the molten salt. The possibility of electrolysis in the nitrate form was also considered. Final purification by vacuum distillation was proposed.

Several areas requiring investigation are immediately recognized: (1) preparation of the feed, (2) the possibility of electrolysis of the nitrate or other melts, (3) conversion to chloride, (4) behavior of fission products during electrolysis. Fullam reviewed these problems in the preliminary study. His conclusion was that dissolution of the salt cake and removal of insolubles would not be a problem. The dissolver solution would then contain substantial amounts of oxygen containing anions other than nitrate and nitrite, specifically sulfate, phosphate and carbonate. These would have to be removed before the salt mixture is fed to the electrolytic cell. It is unlikely that the sulfate could be reduced to an acceptable level using calcium alone and barium addition would probably be required. Calcium or barium addition would also serve to remove most of the fluoride in the solution if the pH is not too low. However, removal of fluoride from the electrolyte is not critical. Phosphate removal would be more difficult since most phosphates of the alkaline earth metals have a slight solubility at the pH of interest. Precipitation of the phosphate as magnesium ammonium phosphate may be required in order to obtain the required phosphate removal. Acidification of the dissolver solution with hydrochloric acid should effectively remove the carbonate but would also precipitate the aluminum. The aluminum concentration varies over a wide range, and with those solutions having a high concentration handling this precipitate may be a problem.

4.1 Nitrate Electrolysis.

It was suggested in Hill's report that several advantages would result from the use of nitrate as the electrolyte melt. Oxygen containing impurities, such as sulfate and phosphate, might have a far less deleterious effect on a nitrate cell operation as compared to a chloride cell. Substantially higher levels of contamination could probably be tolerated without adversely affecting cell operations significantly. Preparation of the cell feed material would be greatly simplified if a nitrate cell were used since the chlorination step would be eliminated. It has been reported that metal can be obtained by electrolysis of the nitrate melt.⁽²⁰⁾ A number of problems do appear, however; (1) the physical properties of the nitrate melt may not be as desirable as for the chloride, e.g., higher viscosity and surface tension and a much lower specific conductance;⁽²¹⁾ (2) thermal decomposition of sodium nitrate produces oxygen and oxides of nitrogen. These will react with sodium metal. In addition, the melt composition will be modified; and (3) side reactions can occur which reduce the sodium yield and the cell efficiency. If the following reaction were permitted to reach equilibrium, $2\text{Na} + \text{NO}_3^- \rightleftharpoons \text{Na}_2\text{O} + \text{NO}_2^-$, then the predominant species would be Na_2O and NO_2^- .⁽²²⁾ Actually, other exothermic reactions can occur such as

ΔG for this reaction is -173.7 kcal; thus, the reversibility of the former reaction may not be real and sodium would exist only if protected by a layer of Na_2O .^(23, 24)

It is not likely that the advantages of the nitrate system will outweigh the disadvantages including the large amount of development work that would be required. Actually there remains a real doubt as to whether the electrolysis is even feasible.

4.2 Hydroxide Electrolysis.

Prior to the advent of the Downs cell for production of sodium metal by electrolysis of sodium chloride, commercial production employed

electrolysis of molten sodium hydroxide. The major drawbacks to this approach are that the sodium hydroxide must be quite pure, and that about half of the current is consumed in electrolyzing water (evolving hydrogen and oxygen). An advantage to the process is the lower temperature of operation (about 315°C).

4.3 Chlorinator Feed Preparation.

Electrolysis of the chloride melt using the Downs cell is an established process. If a reasonably pure feed of sodium chloride can be obtained, the technology for producing sodium metal is well developed. It is assumed, at this point, that distillation will serve as a final purification of sodium. Thus, the major task is the preparation of sodium chloride feed. Roughly the proposed procedure, after removal by precipitation of SO_4 , PO_4 , Ca and Al, is evaporation followed by chlorination with Cl_2 . This task was investigated experimentally and is reviewed in this report.

The Hanford high level wastes vary considerably in composition and flow sheet modifications would be required for the differing compositions. For salt cakes containing appreciable amounts of aluminum it is unlikely that any reagent addition is necessary for phosphate removal since AlPO_4 is quite insoluble except in strongly acidic or strongly basic solutions. Sulfate removal by precipitation as CaSO_4 is not likely to be satisfactory because of its moderately high solubility. Specifications for sulfate content of Downs cell feed could not be found, but in the commercial production of sodium, BaCl_2 or BaCO_3 is used for purification of the NaCl . The present cost of technical grade BaCl_2 is about \$200/ton. Hence, the cost would amount to about \$10-15/ton of salt cake of the composition shown in Table III. An alternate method of SO_4^{2-} removal is to chlorinate in the presence of carbon. This is discussed below.

The aqueous portion of the flow sheet proposed by Hill (2) (except for SO_4^{2-} removal by precipitation which is straightforward if Ba^{2+} is used) was tested since the volumes of the "waste insolubles" and Al(OH)_3 "filter cake" proposed appear unrealistically small. A homogeneous simulated salt cake of composition proposed by Hill as "typical" (except

for having been heated to 180°C to remove water) and as shown in Table III, was used. The gelatinous hydroxides were removed from the solutions by thorough centrifugation instead of filtration and some of the wash solutions were backcycled to minimize solution volumes. Figures 4 and 5 illustrate the flow sheet experimentally used (on a 40g scale) along with the solution volumes required and the solid volumes produced. The starting basis is 2685 kg of dry salt cake which is equal on a dry salt basis to that used in the flow sheet proposed by Hill and quantities are thus directly comparable to his proposed flow sheet. It should be noted that the measured density of the dry simulated salt cake is almost identical to that proposed by Hill for material containing 40% water. His density is too high for such high water content salt.

It is quite apparent from Figures 4 and 5 that the volumes of both the initial waste insolubles and the aluminum hydroxide precipitate are much greater than had been assumed. Thus, the combined volume of these wastes in the wet state is over five times that proposed or 2-1/2 times the volume of the original dried salt cake. This is not surprising in view of the gelatinous nature of these hydrous oxides. Filtering of such large quantities of highly radioactive gelatinous and difficultly washed precipitates can be expected to be a difficult engineering problem. These gelatinous materials are largely water and their volume (and particularly weight) are reduced considerably by drying. The combined waste insolubles and aluminum hydroxide filter cake after drying at 140°C and crushing have a volume about 50% that of the original dried salt cake or 2-1/2 times that proposed by Hill. These dry solids were then pressed at 20,000 psi and their volume measured by displacement in acetone. The pellets of the waste insolubles held together moderately well but the dried Al_2O_3 pellets crumbled and cracked rather severely on pressure release. The acetone displacement volume was about 23% of the volume of the original salt cake, but since acetone penetrated cracks and pores in the pellets and between broken particles, a more realistic volume for the combined dry wastes pressed at 20,000 psi would be about 30% of the volume of the original dried salt cake. The volume of solid would be expected to be somewhat greater if sulfate had been removed as BaSO_4 along with the $\text{Al}(\text{OH})_3$. The volume of final salt solution to

FIGURE 4. MINING STEP

FIGURE 5. REMOVAL OF ALUMINUM AND PHOSPHATE

evaporate (Figure 5) is equal to that proposed by Hill and could undoubtedly be reduced somewhat further by further backcycling of wash solutions or by dissolving new salt cake in backcycled wash water. It should be noted that in order to achieve this final salt solution volume, less water was used to dissolve the original salt cake than Hill proposed.

4.4. Chlorination.

The chlorination of NaNO_3 , NaNO_2 , Na_2O , and Na_2O_2 (the latter two being thermal decomposition products of the first two) can be expected to proceed according to the reactions:

Insufficient thermodynamic data are available to calculate accurate free energies for all of reactions (1) to (4). The free energy for reaction (3) is quite negative (about -40 to -45 kcal/mole) at all temperatures from 25°C to 1000°C. The free energy of reaction (4) is also presumably quite negative over this entire range since Na_2O_2 becomes unstable relative to Na_2O above about 660°C and would thus be of only minimal stability relative to Na_2O below this temperature. Thermodynamic data for NaNO_2 is quite limited, but it appears that ΔG for reaction (2) is definitely negative from 25 to 1000°C and should be as negative as about -30 kcal/mole at 825°C. For NaNO_3 there are fairly complete thermodynamic data (heat capacity data are somewhat limited) and for reaction (1) approximate values of free energies of reaction are:

<u>t °C</u>	<u>ΔG</u>
25	7.95 kcal/mole
225	-2.1
325	-4.9

(continued page 21)

<u>t °C</u>	<u>ΔG</u>
425	-8.3
625	-14.9
825	-21.8

Thus, from the thermodynamic standpoint, chlorination of NaNO_3 , NaNO_2 , and their decomposition products should proceed readily above the 801°C melting point of NaCl if thorough contact of the Cl_2 with the salt can be achieved. The free energy of reaction (5) becomes negative above about 500°C and thus the chlorination reactions are driven even more strongly to the right due to dissociation of NO_2 at these temperatures. Some formation of NOCl can be expected depending on the relative amounts of Cl_2 and O_2 in the gas and on the temperature. Equilibrium constants for reaction (6) are:

<u>t °C</u>	<u>K</u>
25	3.0×10^{-3}
225	5.7×10^{-2}
625	0.42
825	0.66

Experimentally it was found that the chlorination of NaNO_3 begins to occur at an appreciable rate at about 550°C . At 600°C chlorination proceeds moderately rapidly. If Cl_2 is bubbled through molten NaNO_3 at this temperature, NO_2 evolution proceeds at a steady rate for about 40 minutes and after about 60 minutes the NaCl formed has so completely solidified the melt that further reaction is virtually impossible. Because of this, the chlorination would almost certainly need to be carried out above the 801°C melting point of NaCl . At 850°C the chlorination of NaNO_3 is rapid and complete. One run was made in which the NaNO_3 was placed in a preheated furnace at 850°C and a rapid Cl_2 flow through the melt was maintained. Evolution of NO_2 was complete 20 minutes after it started, and the chlorination was terminated 30 minutes after the NO_2 had become

noticeable. Analysis of the NaCl product indicated that it was neutral, and that it contained $<0.01\%$ residual NO_3^- plus NO_2^- .

At 850°C , NaNO_3 decomposes moderately rapidly to Na_2O and Na_2O_2 (Na_2O_2 also decomposes to Na_2O at this temperature). Since in large scale operation heating of the salt to $>800^\circ$ may be rather slow, appreciable amounts of sodium oxide and peroxide may be formed before chlorination starts. To test this, a sample of NaNO_3 was placed in a furnace at 550°C and heated to 850°C over a period of one hour. Evolution of NO_2 was noticeable at 660°C , became appreciable at 800°C , and appeared (from gas color) to be finished 20 minutes after reaching 850°C . Chlorination for 30 minutes at 850°C resulted in a NaCl product which was neutral indicating that the chlorination of sodium oxides produced by NaNO_3 decomposition is also rapid.

The above results indicate that the chlorination of NaNO_3 - NaNO_2 is rapid and complete at 850°C . Rather severe problems with this chlorination do occur though. The corrosiveness of the system is severe. NaNO_3 and NaNO_2 begin to decompose above about 750°C producing a mixture of sodium oxide and sodium peroxide, the latter also decomposing to Na_2O . Sodium peroxide fusion has long been used for breaking difficult and refractory analytical samples and very few materials (including Pt) are resistant to it. Both it and Na_2O are very basic and rapidly attack any acidic crucible materials such as glass, silica, silicates, etc. Magnesia was expected to be resistant to such a melt as well as to chlorine, and magnesia crucibles were used in this phase of the work. Magnesia tubes for Cl_2 addition could not be obtained and fused alumina was used for this purpose despite the fact that it would be expected to react with Na_2O to form NaAlO_2 . The fused magnesia crucibles, although apparently not chemically attacked by sodium oxides, were unsatisfactory because they are not very resistant to thermal shock and tended to crack. They are also rather porous and leakage through the crucible apparently resulted in loosening of the sintered grains of the ceramic. The result was crucible leakage and occasional crumbling of the crucibles. The chlorine sparge tube made of low porosity fused alumina underwent a very slow and uniform surface corrosion. Because the alumina is much less porous and much more resistant to thermal shock, it appears to actually be a much better material of construction even though it is

slowly attacked. Work carried out later on the thermal decomposition of NaNO_3 using alumina crucibles indicated that they are more satisfactory than magnesia crucibles. Whether either an alumina or a magnesia lined reactor would be satisfactory on a large scale will require more studies. All the NaCl products, when dissolved in water, contained varying amounts of turbidity and this turbidity appeared from qualitative tests to be Mg compounds, presumably MgO from some flaking of the surface. Whether such solids would affect Downs cell feed is not known.

One further problem is that NaCl has a vapor pressure of about 2.5 mm at 850°C and CsCl is even more volatile so that the chlorination off-gas stream will contain some radioactive fume. Although no fission products were used in these experiments, it would appear almost certain that all ^{129}I would be converted to I_2 and volatilized during chlorination so that off-gas removal of it would be necessary.

It is possible to convert both sodium sulfate and sodium phosphate to NaCl by chlorination in the presence of carbon. The reactions give, in the case of the sulfate, SO_2 and/or S and, in the case of phosphate, presumably oxychlorides, all volatile at 850°C . Experiments with pure Na_2SO_4 indicated that, at 950°C , the chlorination was exothermic and proceeded rapidly in the early stages, but the last traces (Ba^{2+} test of SO_4^{2-}) were difficult to remove. One very small scale test with phosphate indicated essentially complete removal, but as noted, with Al^{3+} containing feeds little phosphate should get to the chlorination step. Excess carbon (finely divided) could be burned out of the NaCl with about 15 minutes of air sparge at 950°C .

The salt produced from simulated salt cake by the procedure shown in Figures 4 and 5 was chlorinated at 850°C for one hour, excess carbon was added and chlorination was continued for 30 minutes. The carbon was then burned out by a 20 minute air sparge while the temperature was increased to 930°C . The neutral NaCl product contained 15 ppm PO_4^{3-} representing $8.1 \times 10^{-4}\%$ of that originally present and 0.32% SO_4^{2-} representing 13.9% of that present in the original salt cake. The phosphate was no doubt removed by the $\text{Al}(\text{OH})_3$ precipitation, and the sulfate could no doubt

be taken to much lower levels by longer chlorination. Although this is a possible route to SO_4^{2-} removal, the longer chlorination times required, the higher temperature oxidative removal of excess carbon, and the fume problems associated (NaCl has a vapor pressure of 9.5 mm at 950°C) probably make such a route of questionable value in comparison to aqueous BaSO_4 precipitation along with the $\text{Al}(\text{OH})_3$.

No attempt was made to remove fluoride, and there is no indication that its presence would hinder Downs cell operation.

4.5 Sodium Chloride Electrolysis.

The Downs cell, which utilizes an electrolyte of molten sodium chloride and calcium chloride, has been used for many years to produce sodium metal on an industrial scale. Regardless of this fact, however, there is very little detailed information on cell operation available in the literature. Some information is available on European Downs cell practices. Table V summarizes published operating data available on European Downs cell operation. American operating conditions should not be significantly different except for the electrolyte composition. In the United States an electrolyte composition of 66-67% CaCl_2 and 33-34% NaCl is reportedly used. (25) Cell operating temperature is about 600°C .

Evaluation of available data on Downs cell operation points out a number of problems relating to the use of the cell for the proposed application. These problems are summarized below.

1. The interference of oxygenated salts or water in the electrolyte was mentioned in 4.3. When sulfate and water are present, several harmful effects result: (a) oxygen is formed at the anode and anode corrosion is greatly increased, (b) metal fog formation is increased, (c) soluble secondary compounds are formed which, in turn, are decomposed electrolytically initiating a cycle which can reduce the current efficiency for metal production to a very low level, and (d) the overall sodium metal recovery is greatly reduced for a given cell design. (26)

2. The Downs cell is difficult, if not impossible to operate on a small scale. Only industrial size cells have been operated successfully.

TABLE V

DATA FOR EUROPEAN DOWNS CELL OPERATION⁽²⁰⁾

	<u>24,000 amp. Cell</u>	<u>32,000 amp. Cell</u>
<i>Production</i>		
Sodium metal per day	385 kg.	515 kg.
Chlorine per day	590 kg.	790 kg.
<i>Electrolyte</i>		
Calcium chloride	58-59%	58-59%
Sodium chloride	42-41%	42-41%
Current efficiency	78%	-
Voltage, starting	5.7 V.	-
Voltage, final	6.0 V.	-
Sodium per kWh. without copper loss	88.2 g.	-
Sodium per kWh. including copper loss	87.2 g.	-
Calcium chloride usage per 100 kg. sodium	4.0 kg.	-
<i>Cells</i>		
Material of construction	Steel, acid-proof brick lined	Steel, acid-proof brick lined
Dimensions of steel shell (inside)	1620 mm. diam. x 2010 mm. depth	1620 mm. diam. x 2307 mm. depth
Brick lining, Durex II (acid proof brick): thickness	105 mm.	105 mm.
Insulation	40 mm	40 mm.
Overall cell height (bus bars to sodium collector)	3798 mm.	4345 mm.
Cell temperature	585-595°C.	-
Sodium collector temperature	200-250°C.	-
<i>Anodes</i>		
Material of construction	Graphite	Graphite
Length	1464 mm.	2029 mm.
Cross section, each piece	254 x 284 mm.	410 x 410 mm.
Approx. weight	1200 kg.	2130 kg.
Number	8	4
Diameter inside cell	840 mm.	690 mm.
Current contact height	280 mm.	406 mm.
Sealing surface through steel height	180 mm.	322 mm.
Graphite consumption per kg. of sodium	1.6-1.9 kg.	-
<i>Cathodes</i>		
Material of construction	Cast steel	Cast steel
Outside diameter	995 mm.	1066 mm.
Inside diameter	914 mm.	966 mm.
Height	864 mm.	1150 mm.
Cathode current density	9700 amp./m. ²	9700 amp./m. ²

TABLE V (Continued)

DATA FOR EUROPEAN DOWNS CELL OPERATION (20)

	<u>24,000 amp. Cell</u>	<u>32,000 amp. Cell</u>
<i>Diaphragms</i>		
Material of construction	16 mesh iron and steel	16 mesh iron and steel
Outside diameter	876 mm.	926 mm.
Height	939 mm.	1208 mm.
Life, in days	20-30	-

This would make laboratory or pilot scale testing of the proposed process, using a Downs cell, very difficult.

3. The useful life of a Downs cell is reported to be less than one year, at which time it is discarded. This means large volumes of contaminated equipment would be generated by the process. (22)

4. Successful operation of a Downs cell requires a diaphragm between the anode and the cathode. The useful life of the diaphragm is less than 30 days, and it must be replaced at regular intervals to maintain cell efficiency. This continual maintenance item could be a problem when working with contaminated equipment. Whenever the diaphragm is changed, it is standard practice to filter the electrolyte through a steel mesh filter. This is accomplished by air lifting the electrolyte from the bottom of the cell, using dry air, up to the filter suspended above the cell. The filtered electrolyte is then returned to the cell. The filtering operation serves to remove any insoluble sludge from the electrolyte.

5. The sodium metal produced in a Downs cell at 590-600°C contains up to 6% calcium and 1-2% NaCl. When this metal is cooled to 100-120°C, most of the calcium and NaCl precipitate are removed from the sodium by filtration. The filtered solids are a mixture of calcium, NaCl and sodium with the sodium being the predominant species. The exact composition of this Downs cell sludge has not been reported, but it would represent a sizable waste stream which would have to be processed in some fashion. This sludge volume would be far larger than the 0.05 pound per pound of sodium product assumed by Hill, and would probably be somewhere between 0.15-0.2 pound. A variety of processes have been patented for handling the Downs cell sludge including distillation, (27) dissolution in alcohol, (28) dissolution in sodium hydroxide, (29) and further electrolysis. (30) All of these processes would result in the generation of a larger contaminated waste stream. Returning the sludge to the Downs cell has been studied, (31, 32) and may offer the simplest solution to the problem providing it would not seriously hamper cell operations.

There is no reason to assume that the Downs cell process could not be adapted to produce sodium metal from salt cake. It is probable,

however, that electrolysis will reduce most of the radioactive contaminants found in the sodium chloride cell feed. Thus, small amounts of radioactive Sr, Pm, and Ce and most of the Cs would end up in the sodium metal. Removal of these contaminants from the sodium would have to be accomplished in the distillation operation.

Demonstrating the feasibility of the Downs cell process for use in salt cake reduction would require an extensive development program. The principal problem areas would involve:

1. Development of a chlorination reactor.
2. Demonstrating successful metal production and cell operation using feed prepared from salt cake.
3. Determining the path of radioactive contaminants through each step of the process.

5. Sodium Removal by Chemical Reaction.

Thermal reduction processes for the production of sodium have not had commercial significance for the past several decades. The advent of electrolytic processes of high capacity for high purity sodium manufacture have largely excluded continued interest in thermal processes. There exist, however, several methods for the production of alkali metals in general and Hackspill ⁽³³⁾ gives the following list of reactions which may be used for the production of sodium. Some are of little importance and some are reversible under certain conditions:

The chemistry of sodium preparation by reduction is discussed in some detail by Quin.⁽²²⁾ Sittig's text on sodium covers the manufacture of sodium.⁽³⁴⁾ A critical review of reduction processes developed prior to 1922 has been written by Batsford.⁽³⁵⁾ Nearly all the processes described involved some form of carbonaceous material.

The above conditions place severe restrictions on the methods available for sodium production by thermal means. All processes utilizing metal reductant (or their compounds), such as calcium, iron, aluminum, and magnesium yield a solid waste product which must either be processed further to reclaim the original reductant or be discarded as waste. Any reclamation process to recover the reductant requires either electrolytic or chemical reduction of the by-product waste. If the by-product waste is discarded with the remainder of the salt cake waste, one constituent has simply been replaced by another. The only possible benefit of the latter would be in improvement of the waste characteristics required for long-term storage. Because of these problems, it was decided that these processes which constitute most of those discussed by Quin,⁽²²⁾ be eliminated from further consideration.

5.1 Carbon Reduction.

One method of chemical reduction that does offer promise for the production of sodium utilizes carbon to reduce such compounds as sodium carbonate, sodium oxide and sodium hydroxide. In fact, this is really only a modified Deville⁽²²⁾ method of manufacture, which was utilized for the commercial production of sodium prior to inexpensive and available electricity. A relatively recent patent⁽³⁶⁾ describes a

process where sodium carbonate is reduced by carbon in a high temperature reactor, producing sodium vapor and carbon monoxide. When the sodium is condensed, it gives liquid sodium and a sodium carbonate and carbon dross. Fluxing with sodium hydroxide separates the sodium from the dross. The resultant flux is then contacted with carbon monoxide at temperatures greater than or equal to 318°C, producing sodium carbonate which is recycled to the reactor. No yields were reported for this latter method, but for the original Deville process the yield depended largely on the rapid quenching of the distilled sodium vapor before significant reversal of the reaction could occur. The feasibility of the carbonate reduction process is supported by the number of patents granted and by the continued interest of sodium producers (e.g. duPont) in the process. Few details are available, however. Most literature indicates the use of an inert or reducing carrier gas and/or low pressure operation. Temperatures quoted vary from 800 to 1500°C.

Sodium hydroxide is also a suitable feed and good yields (98%) of sodium have been reported by the Soviets ⁽³⁷⁾ for a process utilizing a finely ground carbonaceous material, such as coke, to reduce the hydroxide at 1000°C at a pressure of approximately 1mm mercury. Operating conditions are critical for this method as small pressure variations are said to greatly affect yields and at temperatures of 600-700°C sodium recovery is 20-25%.

The data of Kozhevnikov and Bakhireva ⁽³⁸⁾ indicate two reactions: $3\text{NaOH} + \text{C} \rightarrow \text{Na} + \text{Na}_2\text{CO}_3 + 3/2 \text{H}_2$ at lower temperatures and $4\text{NaOH} + 2\text{C} \rightarrow 2\text{Na} + \text{Na}_2\text{CO}_3 + 2\text{H}_2 + \text{CO}$ at temperatures above 1100°C.

It would appear that Na_2CO_3 , NaOH , Na_2O or other oxides should all be reducible with carbon. Further, it is not likely that most anionic constituents would interfere. Oxidants such as nitrate and nitrite will have to be reduced to a low level; thus, feed preparation for reduction involves thermal decomposition of the nitrate salt. This, along with the carbon-reduction experiments and the volatility of the oxide and/or other sodium compounds must be a part of the study.

A simulated salt cake waste was made up to the composition of Table III. This was evaporated and dehydrated at the melting temperature,

about 250°C. A portion was denitrated by heating it rapidly in an alumina* crucible to 850°C. It was observed that a white solid distilled out of the melt while NO₂ evolution was still strong. Heating was stopped when NO₂ evolution was no longer apparent. At this point a solid "distillate" of about 5-10% of the original weight had been collected. Qualitative tests indicated that the solid was a mixture of sodium nitrite and sodium oxide. This reaction was investigated in more detail later and is discussed in Section 5.2. Although the melt was not nitrate-free, it was used for reduction experiments. Small samples were heated in an argon atmosphere with carbon. With the original nitrate melt, a rapid exothermic reaction took place at 450°C. The denitrated sample apparently reacted smoothly at a higher temperature.

It was helpful to consider the several possible reactions thermodynamically. Free energies were computed for a number of reactions using data from the Bureau of Mines ⁽³⁹⁾ and the JANAF Tables. ⁽⁴⁰⁾ Data are listed in Tables VI, VII, and VIII.

* Samples of various ceramic and metal crucible materials were heated to 800°C with the salt melt. Alumina was found to be the most resistant, easily available material.

TABLE VI

PROPERTIES OF COMPOUNDS OF INTEREST

<u>Substance</u>	<u>mp°K</u>	<u>bp°K</u>	<u>Decomposition Temp. °K</u>
Na	371	1154.5	
Cs	301.9	963	
Na ₂ O	1405	dec	2223
Cs ₂ O	763	dec	--
NaOH	592	1663	
CsOH	545		
Na ₂ CO ₃	1123		
Cs ₂ CO ₃	dec	--	883
NaNO ₃	580		
CsNO ₃	687	dec	
NaNO ₂	544		
CsNO ₂			
Na ₂ O ₂	733		919
Cs ₂ O ₂	867	dec	--
Cs ₂ O ₃	775	dec	
NaO ₂	(825)	(1300)	

TABLE VII

FREE ENERGIES OF FORMATION*

<u>Substance</u>	<u>ΔG_{298}</u>	<u>1000</u>	<u>1200</u>
NaOH	- 90.8 (c)	- 67.5 (l)	- 61.3 (l)
CsOH	- 84.9 (c)		
Na ₂ O	- 89.9 (c)	- 65.7 (c) - 63.3 (l)	58.1 (l)
Cs ₂ O	- 63.7 (c)	(-35) (l)	- 23
Na ₂ CO ₃	-250.4 (c)	-203.3 (l)	-191.3 (l)
Cs ₂ CO ₃	-261.0 (c)		
NaNO ₃	- 87.4 (c)		
NaNO ₂	- 67.8 (c)		
CsNO ₃	- 94 (c)		
CsNO ₂	--		
Na ₂ O ₂		-102.8 (c)	
Cs ₂ O ₂	- 81.9 (c)		
Na ₂ C ₂	- 6.57 (c)		
NaO ₂	(-52.1) (c)	(-29.5) (c)	

*References: (39, 40, 41)

TABLE VIII

FREE ENERGIES OF REACTIONS

<u>Reaction</u>		<u>Free Energy of Reaction, Kcal</u>		
		<u>1500°K</u>	<u>1200°K</u>	<u>1000°K</u>
(1)	$\text{NaOH} + \text{C} \rightarrow 1/2 \text{H}_2 + \text{CO} + \text{Na}$	-11	+9.3	+20. $P_{\text{Na}}=0.018 \text{ atm}$ at 1000°K
(2)	$\text{Na}_2\text{O} + \text{C} \rightarrow \text{CO} + 2\text{Na}$	-19	+6.1	+15.5 $P_{\text{Na}}=.076 \text{ atm}$ at 1000°K
(3)	$\text{Na}_2\text{CO}_3 + 2\text{C} \rightarrow 3\text{CO} + 2\text{Na}$	-11	+45	-- $P_{\text{Na}}=3 \times 10^{-3} \text{ atm}$ at 1123°K (a)
(4)	$\text{Na}_2\text{CO}_3 + \text{C} + \text{H}_2\text{O} \rightarrow 2\text{NaOH} + 2\text{CO}$	- 8.5	+ 7.4	--
(5)	$\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH}$	-15.6	-21.7	-25.9
(6)	$\text{H}_2\text{O} + \text{Na}_2\text{CO}_3 \rightarrow 2\text{NaOH} + \text{CO}_2$		+13.9	+19.5
(7)	$\text{Na}_2\text{O} + \text{H}_2 \rightarrow \text{H}_2\text{O} + 2\text{Na}$			+10.4
(8)	$\text{Na}_2\text{O}_2 + 2\text{H}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{Na}$			- 2.9
(9)	$\text{Na}_2\text{O} + 2\text{C} + \text{H}_2\text{O} \rightarrow 2\text{CO} + 2\text{Na} + \text{H}_2$		+ 4.0	+ 6.4
(10)	$\text{Na}_2\text{CO}_3 + \text{C} \rightarrow \text{Na}_2\text{O} + 2\text{CO}$	+ 4.0	+30	
(11)	$4\text{NaOH} + 2\text{C} \rightarrow \text{Na}_2\text{CO}_3 + 2\text{Na} + 2\text{H}_2 + \text{CO}$	-33.2	+ 1.1	
(12)	$\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$	-21.7	- 9.3	- 1.1

(a) 1123°K = melting point of Na_2CO_3

Some of the conclusions that can be drawn from the data are:

- Any compounds resulting from the denitration of salt cake should be reducible with carbon.
- Although negative free energies are not reached until the temperature is quite high, an appreciable sodium vapor pressure is observed at moderate temperatures.
- The vapor pressure of sodium metal, ~30 torr at 600°C, 130 torr at 700°C is much greater than the calculated vapor pressure of any of the reaction mixtures. Thus, sodium vapor should be easily swept out of the reaction vessel.
- Various reactions such as (11), Table VIII, may occur yielding a portion of the sodium metal while returning the remainder as a more stable intermediate.
- Finally, the formation of carbides, superoxides or compounds not anticipated may change the reactions.

The experimental set-up for the reductions is shown in Figure 6. The greatest difficulty was in designing a condensing system to trap the sodium. The method finally employed used a 1/8 in. diameter stainless steel tube tightly coiled with a tray suspended beneath it. Air passing through the tube kept the temperature below the melting point of sodium. "Mullite" furnace tubes were employed at first but had a short life due to interaction with sodium. Zirconia proved to be an excellent furnace tube material. Iron was also satisfactory. Alumina boats were used (see Section 5.2). Weighed quantities of carbon (powdered charcoal) and the sodium compound were mixed in a uniform layer 3-6 mm deep.

After the reaction was completed, the condensed sodium was washed off with 90% ethanol and titrated with acid.

Thirty-nine experiments were carried out, the variables considered, and their ranges are listed in Table IX.

FIGURE 6. APPARATUS FOR REDUCTION OF SODIUM COMPOUNDS

TABLE IX

EXPERIMENTAL VARIABLES IN CARBON REDUCTION OF SODIUM COMPOUNDS

Feed Materials - NaOH, Na_2CO_3 , CsOH, Cs_2CO_3

Mixtures of these, simulated salt cake (calcined),
simulated salt cake - dehydrated only, $\text{Na}_2\text{CO}_3 + \text{NaNO}_3$

Atmosphere - Argon, 3 torr-760 torr, 5cc/min to 190cc/min.

Time - Temperature - 1-9 hours, max temp 420°C-940°C. Experiments
started at room temperature and brought to final
temperature in 1-3 hours.

Dehydrated ($\sim 250^\circ\text{C}$) salt cake contained far too much nitrate and reacted too rapidly with carbon. The calcined salt cake reacted smoothly and produced sodium metal in a yield of about 40%. Differential thermal analysis (DTA) data, however, showed a sharp exothermal spike at about 500°C suggesting that residual nitrate (or nitrite) was reacting rapidly. A mixture of 93% Na_2CO_3 and 7% NaNO_3 reacted smoothly.

A different type experiment was carried out in which NaNO_3 was first only partially decomposed by heating in an alumina crucible. The NaNO_3 (20g-scale) was held at 850°C for 150 min, which should have left 15-20% of the original combined nitrogen. Powdered carbon was then added to the 850°C melt very gradually. Each minute addition produced extremely vigorous exothermic reaction with considerable white fume evolution. This vigorous reaction continued with each addition until the point was abruptly reached where further reaction did not occur and excess carbon remained in the melt. Thus, although some nitrate can be tolerated, it is probably necessary that NaNO_3 and NaNO_2 be destroyed to a low level before it is safe to proceed with carbothermic reduction on a large scale.

The remainder of the reduction experiments were carried out using pure compounds. The results can be summarized as follows:

A reduced pressure is required. When the reduction was carried out in argon at atmospheric pressure, carbides were apparently formed based on gases released when the residue was dissolved in water. No sodium metal was collected. Pressures of less than 20 torr produced the best yields although somewhat higher pressures could be compensated for by higher argon flow rates.

Reproducible yields were difficult to obtain. The yield, based on metallic sodium recovered, ranged from 20-90%. Low yields were invariably accompanied by low material balances indicating that collecting the sodium vapor remained a major difficulty. This was also indicated by the fact that the length of heating time had little effect on the yield.

The temperature required turned out to be less than that suggested by the thermodynamic data. In one experiment 70% of the sodium in a 1.3g sample

of sodium hydroxide was collected when the reaction mixture was heated to 600°C in a 2 hour interval. The free energy of the reaction at 600°C is calculated to be 26 kcal corresponding to a sodium partial pressure of 2.6×10^{-3} atm. The carbonate seemed to behave similarly to the hydroxide. Slightly higher temperatures may be required for the carbonate reaction.

On the other hand, analogous cesium compounds gave very little cesium metal under the same conditions even though the reactions are thermodynamically more favorable, and the vapor pressure of cesium is higher. In 3 hours at a maximum of 600°C no cesium metal was collected from CsOH and only 17% of the cesium was lost from the boat. A test with Cs_2CO_3 at 700°C gave a 32% yield of metal after 4 hours. In one experiment mixtures of Cs and Na hydroxide gave a sodium enrichment factor of about 2. The explanation for this is probably the formation of interstitial carbide compounds with cesium. Compounds such as CsC_8 , CsC_{24} , etc. with cesium have been reported to be quite stable. (42, 43, 44) Potassium and rubidium also form the interstitial compounds but sodium does not. The compounds decompose stepwise $\text{CsC}_8 \rightarrow \text{CsC}_{24}$ etc., and temperatures above those used in the present experiments are probably required to decompose the lower carbides.

Sodium does form a "normal" carbide, Na_2C_2 , and apparently it is necessary to sweep the sodium vapor out of the reaction vessel to prevent the formation. The various patents that have been filed on methods of sodium manufacture by chemical reduction are largely concerned with removing and trapping the metal.

In summary, while the optimum conditions for the carbon reduction and sodium recovery have not been determined, the feasibility has been established. Many problems remain. Consideration of large scale operation involves questions of materials of construction, methods of sodium condensation to prevent back reactions, feasibility of low pressure operation on a continuous basis, etc. The specific behavior of impurities in the salt cake was not studied in the present work. The maximum concentration of nitrate or nitrite that may be permitted has not been determined. This is discussed in the next section.

5.2 Calcining Studies.

The literature indicates that as NaNO_3 is heated it decomposes first to form NaNO_2 , and at higher temperatures to form Na_2O and Na_2O_2 .⁽²²⁾ Published differential thermal analysis data, along with visual observation,⁽⁴⁵⁾ indicate that, in the region 500–700°C, decomposition of NaNO_3 produces NaNO_2 by the reaction: $\text{NaNO}_3 \rightarrow \text{NaNO}_2 + 1/2 \text{O}_2$, and that between 700 and 830°C several endothermic reactions occur along with evolution of nitrogen oxides which become vigorous by 789°C. These data indicate that the decomposition is complete at about 830°C. Since Na_2O_2 is reported to decompose considerably below 830°C, the product of decomposition was expected to be Na_2O . There are also data on the kinetics of decomposition of sodium nitrate. Three references give data on the rate of the decomposition as a function of temperature^(46, 47, 48) and suggest that the reaction is reversible:

Although these three sources differ in method and particularly in interpretation of the results, they all indicate that reaction (1) is essentially completely at equilibrium within two hours at 700°C. Two of these references^(47, 48) also give values of the equilibrium constant for reaction (1) as a function of temperature, and these are not in agreement. Actual chemical analysis for nitrate and nitrite were used to obtain the data of reference (48) whereas only gas evolution volumes were used to obtain the results of reference (47). The latter authors also used a very questionable crucible material (stainless steel), and it would appear that the results of reference (48) are more likely correct.

There are also detailed data⁽⁴⁶⁾ on the rate of the decomposition reaction:

Experimental rate data for the range 570–760°C are given along with rate expressions, activation energies, and proposed reaction mechanisms. On the basis of these data reaction (2) should reach ninety percent of completion in the times indicated:

<u>Temp., °C</u>	<u>Time for 90% Completion, Min.</u>
700	132
760	33
780	22
850	9

These values are based, for 700 and 760°C on actual rate data presented and, for 780 and 850°C, on extrapolation slightly above the measured range using activation energies given.

The thermal stabilities of sodium oxides in oxygen and in dry CO₂ free air have been studied, ⁽⁴⁹⁾ and it was concluded that NaO₂ decomposes at 120°C in O₂ and 89-90° in dry air to form a series of solid solutions with the limiting compound, Na₂O_{3.60}. This, in turn, decomposes to form Na₂O₂ at 250°C in O₂ and at 215°C in air. The sodium peroxide, Na₂O₂, was reported to begin to decompose gradually at 280°C, to fuse at 510°C, to exist as a heterogeneous mixture with Na₂O between 510 and 545°C, and finally at 545°C to evolve O₂ violently with only Na₂O remaining.

On the basis of the above cited literature data, it was expected that simple heating of NaNO₃, NaNO₂, or crude salt cake waste to 830°C or greater would very rapidly convert all sodium nitrate and nitrite to Na₂O and that even 800°C would probably be sufficient. Experiments on the thermal decomposition of NaNO₃ and NaNO₂ were carried out to determine the minimum temperature required to obtain complete decomposition in a reasonable length of time.

5.3 Thermal Decomposition.

In the first scouting experiment 20g of sodium nitrate were placed in a MgO crucible, and this was, in turn, placed in a long fused quartz, closed end, outer tube, the top of which extended vertically out of a furnace. This was placed in a 600°C furnace, and the temperature increased to 800°C. The first trace of NO₂ in the silica tube was observed at about 780°C. The sample was held at 800°C for 30 minutes at which time NO₂ was still detectable. White fume evolution was observed at 800°C, and

the silica tube above the furnace showed a moderate deposit of this white fume. The furnace temperature was then raised to 850°C and held for 30 minutes. Both NO_2 and white fume evolution were increased over that at 800°C. The temperature was then increased to 900°C and held for 20 minutes. Evolution of NO_2 appeared to decrease somewhat but white fume evolution continued. The furnace temperature was then taken to 950°C, and the presence of a trace of NO_2 , even at this temperature, indicated that the decomposition was slower than expected. The MgO crucible was essentially destroyed indicating that MgO is not a suitable containment material for NaNO_3 decomposition. The weight loss was 13% greater than that predicted for complete conversion to Na_2O . Although some of the loss might have been due to splattering, this, along with the white fume observed, indicated appreciable volatilization which had not been expected.

Another run was made in the same manner except that an alumina crucible was used, and the furnace was initially at 930°C. The sample was held between 930°C and 950°C for about one hour. Most of the sample distilled out of the crucible; only 36% of the initial sodium content remained in the crucible. Thirty two percent of the sodium remaining was present as NaAlO_2 and 0.8% as NaNO_3 .

Because of the excessive volatilization of the melts, further experiments were carried out in deep crucibles, the tops of which were out of the furnace and were lightly covered. Thus, the upper portion of the crucible acted as a condenser and the losses from the crucibles were small, although some loss due to splattering and distillation onto the crucible cover did occur. The results of several decomposition experiments are given in Table X. They are based on dissolution of the melt in water and spectrophotometric analysis for NO_3^- and NO_2^- . One run at 925°C was attempted, but after about 20 minutes the crucible cracked badly, melt leaked into the furnace, and the run was stopped.

TABLE X

DECOMPOSITION OF SODIUM NITRATE

<u>Starting*</u> <u>Material</u>	<u>Temp.,</u> <u>°C</u>	<u>Time,</u> <u>Min.</u>	<u>% of Original</u> <u>Salt Remaining</u> <u>as NaNO₃</u>	<u>% of Original</u> <u>Salt Remaining</u> <u>as NaNO₂</u>	<u>% of Combined</u> <u>Nitrogen</u> <u>Remaining</u>	<u>Crucible</u> <u>Wt. Loss,</u> <u>g</u>
NaNO ₃	700	1070	65.2	30.6	95.8	0.02
"	775	120	54.1	41.0	95.1	--
"	850	100 [†]	13.9	11.8	25.7	0.70
"	"	105	21.9	6.6	28.5	0.82
"	"	240	7.1	0.0	7.1	1.80
NaNO ₂	"	"	6.8	0.0	6.8	1.96

* Initial weights of starting material were in the range 18-25g.

[†] Two periods of about 50 minutes each with cooling between and thus not directly comparable to other runs.

It is quite apparent from the results of Table X that the thermal decomposition of NaNO_3 to NaNO_2 is by no means as fast or complete as indicated by the literature data previously discussed and the calculated rates on page 40. Even at 850°C , where attack of the alumina crucible material is rather severe, the thermal decomposition is unsatisfactorily slow. It is interesting to note that, at 850°C , prolonged thermal decomposition produces the same result whether NaNO_3 or NaNO_2 is the starting material. The fact that only NaNO_3 and no NaNO_2 was observed in the product after prolonged decomposition at 850°C is also surprising. This was highly unexpected based on the literature values ^(47, 48) for the equilibrium constant for reaction (1) as a function of temperature or from the information reported on the decomposition of sodium nitrite. ⁽⁴⁵⁾ It should be noted though that at 700°C the results obtained here agree reasonably well with the value for the equilibrium constant reported in reference 48.

The fact that NaNO_2 is produced early in the decomposition, but that NaNO_3 remains even after extended heating at high temperatures may suggest that the nitrate does not actually exist in the melt, but that it is re-formed at some time before analysis. One possibility is that NaNO_2 in the melt is reoxidized to NaNO_3 by Na_2O_2 on cooling of the melt. Gas evolution during aqueous dissolution of the frozen melt and qualitative tests for peroxide in the resultant solution indicates appreciable peroxide in the frozen melt even though the literature data indicate that Na_2O_2 would have completely decomposed at 850°C to Na_2O . It was shown experimentally that such reoxidation of NaNO_2 to NaNO_3 could not have been occurring during the aqueous dissolution itself. Another possibility is that a relatively stable peroxyxynitrate forms, which re-forms NaNO_3 upon aqueous dissolution. The melt is deep brown in color, and this changes rather abruptly to pale yellow at or just below the freezing point, and to white at 25°C . A third possibility is that a more thermally stable nitrate species forms in the melt through interaction of NaNO_3 with excess Na_2O , and that this is hydrolyzed back to NaNO_3 on dissolution in water. Both pyronitrate, ⁽⁵⁰⁾ $\text{N}_2\text{O}_7^{4-}$, and orthonitrate, ⁽⁵¹⁾ NO_4^{3-} , have been reported, but their thermal stability is not known.

The thermal decomposition of sodium nitrate is not a simple process. Thermal decomposition at atmospheric pressure will not achieve adequate decomposition in reasonable times at 850°C. At higher temperatures or much longer time periods at 850°C, corrosion of containment materials would be quite severe. Even at 850°C corrosion of alumina is rather severe. This corrosion is, fortunately, quite uniform and results in uniform thinning of crucible walls. It is possible that ZrO_2 crucibles would be somewhat more corrosion resistant, but they were not tried.

5.4 Catalytic or Reductive Decomposition.

It is possible that by the use of catalysts or gaseous reducing agents (which have the advantage over solid or liquid reductants in ease of controlled addition), the decomposition rate of NaNO_3 - NaNO_2 could be increased and the decomposition temperature decreased.

One old and very brief report ⁽⁵²⁾ claims that NaNO_3 is largely decomposed by steam at "just under 600°". We performed one experiment at 850°C in which NaNO_3 was held at 850°C for 85 minutes, following which a steam-air mixture was passed through it for 60 minutes. About 15% of the original combined nitrate remained as a mixture of NaNO_3 and NaNO_2 . This is, within experimental error, approximately the same as the amount expected from thermal decomposition alone indicating no effect of the steam. The melt had a lower freezing point indicating conversion from Na_2O to NaOH by the steam. A similar experiment at 700°C also showed no appreciable decomposition due to the use of steam.

Ethane was tried as a reducing agent at 850°C. Reaction with the melt was rapid with considerable white fume evolution. The alumina gas addition tube plugged after 13 minutes with carbon black due apparently to thermal cracking of the ethane. At this point the experiment was terminated, but insufficient ethane had been added to destroy all the combined nitrogen. Corrosion of the alumina gas addition tube was severe even though it had only been in the melt 13 minutes.

Carbon monoxide has been reported ⁽⁵³⁾ to reduce NaNO_3 slowly above 500°C . Sodium nitrate was held at 850°C for 160 minutes thereby destroying about 85% of the combined nitrogen. Carbon monoxide was then passed through the melt via an alumina tube. An appreciable amount of white to slightly yellowish fume was evolved. After 11 minutes the off-gas burst into flames, and did so repeatedly when extinguished. At this point, carbon deposition on the crucible walls became apparent and CO addition was stopped after a total time of 15 minutes. The frozen melt contained some carbon but no detectable nitrate or nitrite indicating complete and rapid reduction at 850°C . Corrosion of the alumina gas addition tube and of the bottom of the crucible at the point where gas addition was made was severe. About 2.5 mm of the end of gas addition tube was completely removed and another 7 to 8 mm was markedly thinned. The most likely explanation at present for this severe and rapid corrosion appears to be high local temperature.

At 700°C , carbon monoxide addition for 42 minutes did not produce experimentally detectable reduction. At 775°C , about 15% of the combined nitrogen was destroyed in 11 minutes and about 50% was destroyed in 55 minutes; corrosion of the alumina was not severe. Further experiments were not carried out, but it can be concluded that complete reduction of NaNO_3 and NaNO_2 can be achieved with carbon monoxide, but that temperatures in the range 775 to 850°C are required. This should produce a material containing largely Na_2CO_3 for carbothermic reduction.

It should be noted that, in one experiment with carbon monoxide reduction at 775°C , a mild explosion occurred which blew out most of the melt. This occurred after several minutes of gas flow, and the mechanism could not be determined. It appears most likely that this was due to liquid or solid organic material or possibly water from the gas tubing or gas regulator being carried into the bottom of the melt. No mechanism for such a sudden reaction with CO seems possible, and there was no evidence at this temperature of carbon being formed in the gas addition tube through the reaction $2\text{CO} \rightarrow \text{C} + \text{CO}_2$ although this does occur to some extent at 850°C .

Ammonium salts react with nitrates at low temperature producing N_2O . This reaction was confirmed by both open crucible experiments and by DTA experiments using ammonium sulfate. This reagent, of course, adds solid to the waste. One experiment, using NH_3 gas, bubbled through the melt at a relatively low temperature, $<400^\circ C$, did not produce N_2O . The reaction was not investigated further.

Another logical reducing agent would be hydrogen, presumably diluted with inert gas. This was not tried experimentally. The product of hydrogen reaction would be expected to be principally $NaOH$. It has also been reported that certain oxides, including particularly V_2O_5 ,⁽⁵⁴⁾ catalyze the thermal decomposition of $NaNO_3$. Although these add solids to the waste, it might be that only very small amounts would be needed to markedly improve the thermal decomposition rate.

5.5 Volatilization of Sodium Compounds.

The excessive volatility of sodium nitrate melts noted in Section 5.1 and described above is an interesting phenomenon in itself. Several experiments were made in an attempt to determine the reaction occurring. Sodium nitrate samples of about 5g each in alumina crucibles were heated in a quartz tube. For experiments using a flowing gas (or vacuum) a small alumina tube led to a bulb and glass wool filter to trap the solid formed. Table XI lists the conditions and observations. The experimental results can be briefly summarized:

- (1) A large fraction of the solid vaporizes at temperatures well below those reported for sodium compounds. Volatility is obvious at $650^\circ C$.
- (2) The solid product that is collected is primarily sodium nitrite but contains sodium nitrate and sodium oxide.
- (3) The solid, which forms in the gas phase, is extremely fine and will carry through several feet of tubing at low gas flow rates.
- (4) The residue is sodium nitrate-sodium nitrite in a ratio of about 3:1 or greater.

(5) A temperature as low as 720°C is adequate to produce a large amount of product. A one hour heating time from ambient to 800°C may result in an 80-90% weight loss.

(6) A mixed sodium nitrate-cesium nitrate melt gave a volatile product enriched in cesium.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) experiments were also carried out. Figure 7 shows typical DTA data for sodium nitrate, sodium nitrite, and the simulated dried salt cake, heated in helium. The salt cake shows the characteristics of sodium nitrate. The reactions in the vicinity of 800°C are quite complex and not always reproducible. When heated in oxygen, less fine structure was observed. With NaNO_2 in oxygen an exothermic reaction occurred between 600 and 700°C, and the high temperature portion of the curve resembled somewhat the NaNO_3 decomposition. TGA curves in helium at one atmosphere showed little difference between NaNO_2 and NaNO_3 . A steady weight loss began at about 600°C and reached a maximum rate at about 800°C at which point 50% of the sodium had volatilized. At 950°C only 10% remained. Another set of TGA experiments was carried out under vacuum conditions, <2 torr. At temperatures from 500 to 600°C, 95 to 99% of the sodium nitrate or sodium nitrite was distilled out in times ranging from 8 to 170 min. The "distillate" collected was a mixture of sodium nitrate, sodium nitrite and sodium hydroxide. Of the common sodium compounds none has, on first consideration, sufficient volatility to account for the observed results. Sodium metal is the only material with a reasonably high vapor pressure, 0.135 atm at 700°C. (55) The possibilities are: a) the nitrate or nitrite decomposes some way to give metal and oxides of nitrogen which distill and recombine, b) the nitrate or nitrite volatilizes unchanged, c) an unsuspected sodium compound with a high vapor pressure is formed. The first is thermodynamically unreasonable. Brewer and Margrave have carefully measured the vapor pressures of Na_2O (56) and found that the vapor pressure of Na_2O agrees very closely with that calculated from thermodynamic data for vaporization occurring as free Na and O_2 through the reaction $\text{Na}_2\text{O} \rightarrow 2\text{Na} + 1/2 \text{O}_2$.

TABLE XI

EXPERIMENTAL THERMAL DECOMPOSITION OF SODIUM NITRATE

<u>Experiment</u>	<u>Material and Conditions</u>	<u>Temperature, °C, & Observation</u>	<u>Results</u>
1	Simulated salt cake in static air	500° -NO ₂ evolution begins, 700°- white solid condenses, 800°- NO ₂ ceases	Residue NaNO ₂ -NaNO ₃
2	"	3 hrs at 800°	NaNO ₂ -NaNO ₃ residue, 42% wt. loss
3	NaNO ₃ , argon stream	700-740°, 800° at end	Wt. loss 88%
4	Same	4 hr. heating to 730° max.	Wt. loss 34%
5	Same	5 hr. heating to 780° max.	Wt. loss 84%
6	80% NaNO ₃ , 20% CsNO ₃ Argon stream	5 hr. heating to 780° max.	Wt. loss 86%. Residue 3:1 NO ₃ ⁻ : NO ₂ ⁻ . Cs enrichment factor in vapor 2.8-3.2
7	NaNO ₂ argon stream	3.5 hr. heating to 750°	Wt. loss 70%. Residue 4:1 NaNO ₃ :NaNO ₂
8	NaNO ₃ , NO ₂ gas stream	4 hr. heating to 890°	No white fumes or powder seen until >850°. Powder collected is 2:1 NaNO ₂ :NaNO ₃ 65% wt. loss. Residue is NaNO ₃ :NaNO ₂ >1.0.
9	NaNO ₃ , vacuum (1-3 torr)	3.5 hr. heating to 890°	Wt. loss 95%. No NO ₂ ⁻ or NO ₃ ⁻ found in residue.

FIGURE 7. DTA CURVES FOR SALT DECOMPOSITION

The vapor pressure of sodium over Na_2O in air is, from these data, 6.7×10^{-7} atm at 850°C and 8.2×10^{-5} atm at 950°C , much too low to account for the volatilization. Either b) or c) is a possibility. For the latter, the higher oxides could be considered. If the estimated boiling point of NaO_2 from Table VI is used, the vapor pressure at 700°C is calculated to be 1.0×10^{-2} atm which is about 1/13 that of sodium metal. Mechanism b) is supported by the fact that the salts could be vaporized at a relatively low temperature in the TGA experiments. Further evidence is the data of Hardy and Field.⁽⁵⁷⁾ They were able to distill the alkali metal nitrates and nitrites at 350 to 445°C at pressures of 5×10^{-3} torr. They postulate the existence of ion pairs in the vapor state.

Although the volatilization of a sodium compound is a problem in preparation of calcined feed for reduction studies, the ease with which it occurs suggests that it be considered as an alternative method for sodium removal.

V. PURIFICATION OF SODIUM.

Sodium metal produced from salt cake will contain radioactive contaminants. The process or processes used to produce sodium will provide some decontamination. Conservatively, however, it must be assumed that an appreciable fraction of most of the nuclides in Table IV will be present. The carbon reduction process would be expected to produce reasonably clean sodium and cesium and iodine might be the main contaminants.

1. Distillation.

Various methods of removing these contaminants were considered; the one method deemed most likely to be feasible for the separation of all the contaminants was fractional distillation of the metallic sodium after it is produced (by electrolysis or by carbothermic reduction).

In Table XII are listed the data pertinent to the distillative separation of the elements requiring the highest degree of separation from the sodium. The relative volatility values were calculated for the boiling point of sodium from the equations given by Castleman⁽⁵⁸⁾ in his review of the behavior of fission products in metallic sodium. The minimum

number of stages required were calculated for the theoretical case of distillation at an infinite reflux ratio and are thus useful only for illustrative purposes; the actual number of stages required will be greater than this by a factor that will depend on operating conditions. As can be seen, separation is required from a more volatile contaminant (cesium) as well as from less volatile contaminants; this necessitates a two-step distillation procedure.

The less volatile contaminants that will be most difficult to separate are seen to be iodine (if present in the sodium) and strontium. Conditions that provide adequate decontamination from these elements should also provide adequate decontamination from the other contaminants that are less volatile than sodium. The number of theoretical stages required to effect the desired decontamination from strontium and iodine was calculated (by the McCabe-Thiele method) for various operating conditions; the results are presented in Table XIII. It is seen that achieving a decontamination factor of 1×10^3 from iodine is somewhat more difficult than achieving a DF of 1×10^9 from strontium.

Distillative decontamination from iodine may not be necessary with sodium prepared in a Downs cell since significant separation should occur in the chlorination and electroreduction steps. With sodium prepared by carbothermic reduction, however, iodine could well be the limiting less volatile contaminant.

Distillative decontamination from strontium may be easier than indicated by the data of Table XIII due to the formation of relatively nonvolatile SrO . Clough ⁽⁵⁹⁾ has calculated that the strontium oxide to strontium metal ratio would be of the order of 10^8 in sodium containing only 2.7 ppm Na_2O and found little if any volatility of strontium from sodium containing 15 ppm oxygen. The presence of oxygen could also decrease the volatility of some of the other less volatile contaminants, but does not affect the volatility of iodine ⁽⁶⁰⁾ and would not be expected to affect the volatility of cesium.

The separation of the more volatile contaminant, cesium, from the sodium is expected to be the most difficult to achieve. This is largely

TABLE XII
VOLATILITY OF SODIUM CONTAMINANTS

<u>Element</u>	<u>Boiling Point (°C)</u>	<u>Volatility Relative to Sodium (b)</u>	<u>Required Decontamination Factor (c)</u>	<u>Minimum Number of Stages Required (d)</u>
Cs	670	10	2×10^7	9.3
Sr	1150	0.058	10^9	18.9
I ^(a)	1300	0.32	10^3	10.2
Sb	1380	0.000013	7×10^5	1.6
Ce	1400		10^7	
Sm	1900		10^4	
Am	2600		8×10^3	
Cm			6×10^3	
Co	2900		2×10^3	
Pm	~2900		10^6	
Pu	3230		3×10^4	
Ru	4150		4×10^5	

(a) Present as NaI

(b) Calculated for the boiling point of sodium from data in reference (58)

(c) From Table IV

(d) For a 1% waste loss with an infinite reflux ratio

TABLE XIII

THEORETICAL STAGES REQUIRED FOR Sr AND I REMOVAL

Bases:

- Feed = liquid sodium at its boiling point
- Strontium $\alpha = 0.058$; Required DF = 1×10^9
- Iodine (NaI) $\alpha = 0.32$; Required DF = 1×10^3

<u>Relative Flow</u>				<u>Theoretical Stages Required</u>	
<u>Feed</u>	<u>Product</u>	<u>Waste</u>	<u>Reflux</u>	<u>Strontium</u>	<u>Iodine</u>
100	90	10	90	11	16
100	99	1	99	12	19
100	99	1	30	16	Inoperable
100	99	1	10	36	

caused by the probable need for employing isotopic dilution with inactive cesium to attain adequate decontamination from the radioactive ^{137}Cs . At a DF of 2×10^7 the concentration of ^{137}Cs in the purified sodium would be about 10^{-6} ppm; at such an extremely low concentration, it is doubtful that the more volatile cesium could be distilled from the sodium, since "When the volatile metal has a low diffusivity and is sufficiently depleted, the concentration of the volatile metal at the surface may become so low that metals are evaporated in nearly the same ratio as they occur in the residual metal." (61) The low concentrations of the contaminants less volatile than sodium should pose no problem since here the sodium is evaporated away from the contaminants.

The cost of the cesium required for isotopic dilution is a function of the required decontamination factor and the concentration of cesium in the purified product (as well as of other factors). At a minimum cesium concentration of 0.5 ppm (which was demonstrated to be high enough for good distillative separation) the cesium cost would be prohibitive unless the separation was performed in multiple columns. Data illustrating the effect of the number of columns employed on the cesium cost are contained in Table XIV. As indicated, these costs assume recycle of the waste streams from one column to the preceding column. For the stated conditions, the cost of the cesium is seen to be unreasonably high if less than three columns are employed. A flow diagram depicting the operation of a three-column array for decontaminating the sodium from cesium by a factor of 2×10^7 is presented in Figure 8.

The number of theoretical plates required to effect the desired separation depends, of course, on the conditions under which the columns are operated. In Table XV are presented results obtained (by the McCabe-Thiele method) for several sets of operating conditions. The optimum operating conditions would be decided by economic considerations; most likely such conditions would fall in the range where 20 to 50% of the sodium would be vaporized and 5 to 10 theoretical stages would be required to attain the decontamination factor of 270 necessary to attain the desired overall decontamination in the three-column array.

TABLE XIV
EFFECT OF MULTIPLE COLUMNS ON Cs COST

Bases:

- ^{137}Cs DF = 2×10^7
- Total Cs concentration ≥ 0.5 ppm throughout
- Waste streams recycled

<u>Number of Columns used</u>	<u>DF required per Column</u>	<u>Cesium addition required (ppm)</u>	<u>Cesium cost^(a) (\$/Kg Na)</u>
1	2×10^7	1×10^7	4000
2	4500	2250	0.90
3	270	135	0.054
4	67	33.5	0.013
5	29	14.5	0.0058

(a) Based on a cesium cost of \$400 per Kg

TABLE XV

THEORETICAL STAGES REQUIRED FOR Cs-Na SEPARATION

Bases:

- Feed = liquid sodium at its boiling point
- $\alpha = 10$

<u>Feed</u>	<u>Flow</u>				<u>Theoretical Stages Required for DF = 270</u>
	<u>Product</u>	<u>Waste</u>	<u>Reflux</u>	<u>Total Vapor (Reflux & Waste)</u>	
101	100	1	100	101	6
101	100	1	40	41	7
101	100	1	20	21	11
101	100	1	12	13	23
101	90	11	40	51	5

FIGURE 8. FLOWSHEET FOR SODIUM DISTILLATION

Sodium prepared by carbothermic reduction may require less purification by distillation than would that produced in a Downs cell because of the formation of relatively nonvolatile cesium-carbon compounds (44) during the reduction step. The data available do not permit a good estimate of the decontamination that might be attained. (See Section 5.1.)

The experimental investigation in the area of sodium distillation involved only the cesium-sodium separation. This study verified that the calculated value of the relative volatility is correct and identified a concentration level (0.5 ppm) above which separative problems caused by low diffusivity and low concentration would be unimportant. The minimum concentration level was not determined; additional studies employing a more sensitive analytical technique could perhaps demonstrate good separation at even lower levels.

The experiments were performed simply by heating cesium-sodium alloys to a temperature at or near the boiling point of sodium, allowing a portion of the alloy to distill away, and comparing the amounts of cesium and sodium that did not distill with those initially present. The experiments were performed in an inert atmosphere dry box, and the cesium analyses were performed by flame emission spectroscopy following cesium isolation and concentration on ammonium molybdophosphate. Cesium analysis by radiochemical techniques would have been preferable but could not be used because of the lack of an inert atmosphere facility that could be used with radioactive materials.

In a simple batch distillation, as was used here, the relative amounts of cesium and sodium distilled are governed by the relationship

$$\ln F_{\text{Cs}} = \alpha \ln F_{\text{Na}}$$

where F_{Cs} and F_{Na} are the fractions of the components remaining undistilled and α is the relative volatility at the temperature of distillation. Results of the three successful experiments are shown in Table XVI. These data verify the value of 10 calculated for α at this temperature from the data of other workers (62, 63) and indicate that, at this temperature, kinetic factors leading to poor separation are not serious at cesium concentrations as low as 0.5 ppm.

TABLE XVI

CESIUM-SODIUM SEPARATION IN BATCH DISTILLATIONS

Temperature near 880°C

Distillation rate ~70 mg/min (~15 mg/min, cm²)

Oxygen content of sodium estimated to be about 50 ppm

Feed			Residue			α (a)	DF (b)
g Na	μ g Cs	ppm Cs	g Na	μ g Cs	ppm Cs		
4.4	48	11	3.2	3	0.9	9	12
7.2	860	120	4.0	1.5	0.4	11	300
5.4	650	120	2.15	<1	<0.5	<7	<240

$$(a) \quad \alpha = \frac{\ln F_{Cs}}{\ln F_{Na}} = \frac{\ln (\mu\text{gCs in residue} / \mu\text{gCs in feed})}{\ln (\text{gNa in residue} / \text{gNa in feed})}$$

$$(b) \quad DF = \frac{\text{ppm Cs in feed}}{\text{ppm Cs in residue}}$$

In an earlier experiment performed at 330°C (under vacuum) with a cesium concentration of about 5 ppm in the starting material, problems caused by low cesium diffusivity did apparently occur. In this experiment, distillation of 43% of the sodium (over a period of two hours) resulted in distillation of only 88% of the cesium. These data yield an α value of about 4 instead of that of 545 calculated for the temperature from the data given by Castleman.⁽⁵⁸⁾ The cesium-sodium alloy used in this experiment was prepared by evaporating a solution of $^{137}\text{CsCl}$ to dryness, adding sodium metal, and allowing two hours at 230°C for the reaction

to occur. While this reaction is not thermodynamically favorable, the large excess of sodium should force it to proceed as written.

2. Other Methods.

Filtration of the molten metal has been studied in the LMFBR program. Oxides have very low solubility in sodium, and it has been reported that cesium is removed with the oxides.

A potential method suggests itself based on information in the present report. The formation of stable interstitial compounds (Section 5.1) between carbon and cesium could be used for cesium removal. Heating the contaminated sodium with carbon followed by filtration would be a simple inexpensive operation and should give good decontamination factors.

VI. CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK.

The general feasibility of salt waste volume reduction by sodium removal has been demonstrated. The process would entail 1) removal of insolubles (including those purposely formed to remove sulfate and phosphate ions), 2) concentration, drying and chlorinating, 3) electrolysis of the molten chloride, and 4) purification of sodium by filtration techniques and distillation. The second and preferred process would eliminate step one. The steps would be: 1) concentrating drying and calcining,

2) reduction with carbon and volatilization of sodium at low pressures, and 3) purification of sodium as before.

The true volume reduction that might be achieved has not been established, but it may be less than the original estimate of Hill.⁽²⁾ If the general concept of sodium removal is to be pursued, then additional laboratory work would be required on the calcining and carbon reduction steps. With the former the high volatility of sodium compounds is yet unexplained. This interesting reaction should be investigated since it affects the calcination step. Also, it conceivably could be employed as a volatility process on its own. Some nitrate or nitrite can be tolerated in the carbon reduction step, but the limit has not been defined. The incomplete destruction of nitrate on calcination may require a chemical additive. Process and equipment design for the reduction step will be a real challenge and will require much more effort on both a laboratory scale and pilot plant scale. Materials of construction research would be a major item.

The sodium purification by distillation appears to be relatively straightforward and is ready for demonstration on a larger scale. Experiments on decontamination by filtration (hot and cold trapping), including cesium removal by interstitial carbide formation should be carried out.

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