

SODIUM WASTE DISPOSAL METHOD

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INTRODUCTION

Operation of Liquid Metal Fast Breeder Reactors will generate radioactive sodium waste which is a hazardous material unsuitable for direct disposal. Federal regulations¹ for burial of radioactive waste exclude metallic sodium as an acceptable waste form because of its chemical reactivity. The regulations state that radioactive waste, to be suitable for burial, must not be capable of explosive reaction with water or with flammable materials in the burial site. Metallic sodium, of course, cannot satisfy either of these requirements because corrosion of the sodium container may eventually allow ground water to react violently with the sodium.

A method was needed to convert sodium to a chemically stable form for disposal. An experimental program was undertaken at Argonne National Laboratory with the objective of developing this method. The approach chosen was controlled oxidation of the sodium to form sodium oxide. The sodium oxide could then be incorporated into a simple high-sodium glass for disposal. The proper composition and characteristics of glasses to be used for this waste disposal were investigated by Blair *et al.*² This work was concerned with development of the method for converting metallic sodium to sodium monoxide.

BACKGROUND

Techniques that have been considered and used previously for sodium removal and disposal include (1) reaction with steam or water vapor, (2) reaction with alcohol, (3) reaction with concentrated caustic solution, (4) alloying with metals such as lead or bismuth, (5) reaction with molten NaOH, (6) reaction with gases such as ammonia, and (7) oxidation (calcining).^{3,4} The advantages and disadvantages of these techniques were evaluated on the basis of process simplicity, ease of product handling, remote operation, and ease of disposal of the product. Controlled oxidation of waste sodium in a calciner was chosen for development. An experimental program was conducted in which process variables were studied to determine their effect on the product.

The term calcining, as used in this report, is the controlled oxidation of sodium to form sodium oxide. In this process, sodium is poured onto a bed of sodium oxide particles at elevated temperatures. The particles are coated with a thin layer of sodium by mixing. Oxygen (as air or $O_2 + N_2$ mixtures) is then directed to the calciner countercurrent to the movement of the bed. The sodium on the bed is oxidized in a controlled manner, and, when the oxidation is completed, a portion of the bed can be unloaded. More sodium is added and the process is continued.

EXPERIMENTAL

The calcining vessel used in these experiments is shown in Fig. 1. The vessel was a 0.21 m³ drum 890 mm high and 560 mm in diameter, constructed of type 304 stainless steel. One end of the drum was removable and contained two penetrations sealed with threaded closures of 50 mm diameter. Rolling rings were attached to the outside of the drum 290 mm from each end. A set of six lifting baffles 50 mm wide x 810 mm long x 3 mm thick were attached to the inside of the drum to facilitate mixing. The calciner body was heated by three resistance heaters equally spaced along the drum. A ceramic fiber insulating blanket was applied to the drum surfaces. Thermocouples were attached to the drum at each heater location to monitor temperature during heat-up. Calciner rotation was accomplished with a roller set driven by a continuously variable D.C. motor.

Rotary seals were welded into the center of each end of the drum to allow entry and exit of gases and introduction of liquid sodium. One penetration allowed introduction of inert gas and/or oxidizing gas. A similar penetration on the other end of the drum allowed two concentric tubes to enter the calciner. Inert gas and/or liquid sodium entered the calciner through the center 12 mm diameter tube. A 5 mm annulus between the tubes provided the gas exhaust from the calciner. The liquid sodium delivery tube was wrapped with a sheathed heater over its entire length and a thermocouple was attached at its outlet tip. Another thermocouple extended downward from the tip into the moving oxide bed.

A reservoir supplied sodium to the calciner as needed and the feed line was wrapped with trace heaters and insulation. The quantity of sodium charged to the calciner was monitored with an electromagnetic flowmeter in the sodium line.

The exhaust gas line was provided with a particulate removal system. Heavier particles were removed from the exhaust gas by deposition in a knock-out (settling) vessel which the gas entered immediately after leaving the calciner. A cyclone separator was mounted in series with the knock-out vessel, and it removed the finer particles from the exhaust gas. Oxygen concentration in the exhaust gas was monitored by withdrawing samples downstream from the cyclone separator and directing them to a gas chromatograph.

The calciner was initially loaded with a bed of Na₂O equivalent to 10% of the drum volume. Subsequent sodium additions and oxidation increased the volume of this bed and when the loading reached approximately 20%, some oxide was removed. An inert gas (N₂ or Ar) purge was continually maintained through the calciner to prevent collection of moisture. To initiate oxidation, the calciner and bed were pre-heated to the desired ignition temperature (120-200°C) while maintaining an inert gas purge. When the proper temperature was attained the heaters were disconnected allowing the drum to be rotated on the roller set. The desired quantity of sodium (3-9% of the bed by weight) was then measured onto the bed. The bed and sodium were then mixed for 15 minutes by rotation at 2 RPM. The

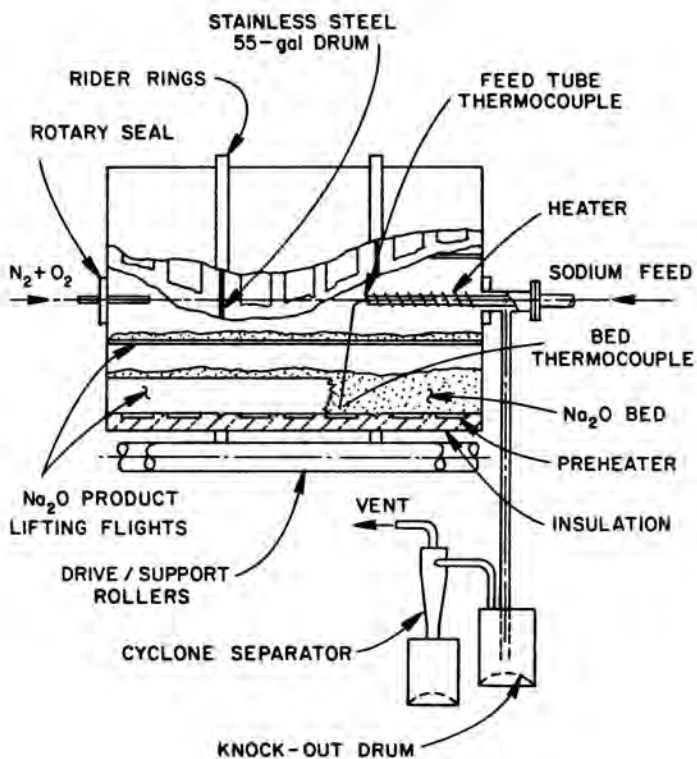


Fig. 1. Calciner schematic.

rotational speed of the calciner was then reduced to 1 RPM and oxygen flow was started through the calciner, initiating oxidation of the bed. Increases in the bed and calciner chamber temperatures accompanied the oxygen introduction. Temperatures in the calciner during oxidation typically peaked between 200 and 290°C with a maximum temperature of 340°C noted during one experiment.

The exhaust gas was sampled and analyzed by the gas chromatograph at approximately 15 minute intervals. When this oxygen concentration increased to a pre-determined level and the bed temperatures began to decline, the reaction was considered to be completed. At this point, the oxidizing gas was shut off, the inert gas flow was continued, and preparations were made for the next sodium addition (or shutdown if this was the last batch).

Numerous chemical analyses were performed before, during, and after each calcining experiment. In addition to the gas chromatographic analyses, samples of the product were taken after the experiments to determine the quantities of elemental sodium and sodium peroxide. For determination of elemental sodium, alcohol dissolution of aliquots of the samples was performed. The solutions were agitated and the gas generated in the dissolution was expanded into a calibrated volume. This gas was sampled and the hydrogen was measured chromatographically. The equivalent amount of sodium present was then determined from the hydrogen analysis.

Product samples were taken from various locations in the bed for sodium peroxide (Na_2O_2) analyses. Aliquots of the samples were dissolved in a chilled bath and were acidified. The solutions were titrated with potassium permanganate to determine the hydrogen peroxide content which was then correlated to the original Na_2O_2 in the sample. The change in concentration of sodium peroxide in the product from experiment to experiment indicated the effect of excess oxygen added during the reaction. Excess oxygen was found to cause formation of Na_2O_2 in addition to Na_2O .

The quantity of oxide particles collected in the exhaust gas treatment system was measured to determine the carry-over rate for the experimental conditions. The influence of experimental parameters on particle size distribution of the product was investigated in some cases by mechanically sieving samples of the calciner bed.

Cesium-137 is a fission product that is expected to be present in most radioactive sodium. Since cesium has a higher vapor pressure than sodium, its behavior during the oxidation process is of concern. Non-radioactive cesium metal was added to the oxide bed prior to one of the oxidation tests. The test was run in the normal way, then samples were taken from various portions of the calciner bed, the exhaust-gas treatment system, and filter papers placed at the gas exhaust. Analyses of these samples for cesium and total sodium were performed to determine the cesium/sodium ratios at these locations.

Table I. Experimental Conditions

Experiment Number	Sodium Loading (wt %)	Oxygen Concentration in Oxidizing Gas (vol %)	Total Gas Flow (L/min)	Initiation Temperature (°C)	Maximum Temperature in Chamber (°C)	Maximum Bed Temperature (°C)	Oxygen Concentration End-Point in Exhaust Gas (vol %)
1*	5	30	21	145	230	205	25
2*	5	30	21	155	230	205	20
3*	5	30	21	150	265	230	23
4*	5	30	21	120	230	210	25
5	6	30	21	130	220	200	24
6*	6	47.3	15.3	168	320	260	24
7	7	47.3	15.3	125	300	235	28
8	7.5	47.3	15.3	155	340	305	20
9*	7.5	30	14.9	155	265	245	9
10	7.5	30	14.9	155	225	210	9
11*	7.5	30	16	125	270	235	2.25
12*	7.5	30	16	125	315	275	2
13*	7.5	30	16	120	295	295	2
14	7.5	Dry Air	17.9	143	210	185	2
15	7.5	Dry Air	16	155	220	205	2
16	7.5	Dry Air	16	170	225	220	2
17	7.5	Dry Air	16	150	215	240	0.8
18	9	Dry Air	16	200	230	240	0.5
19	7.1	25 Rel. Hum. Air	16	173	245	250	1.5
20	5.2	55 Rel. Hum. Air	16	175	215	210	1.0
21	6.5	Dry Air	16	150	205	205	0.8

* Subsequent additions made continuously—calciner always at elevated temperature.

Figures 2 and 3 are representative of the temperature and oxygen concentration variation as a function of time during each oxidation. These plots were selected because they illustrate the effects of high sodium loading (7.5 wt %) and low gas flowrate (14 L/min) on the time required for oxidation of the sodium. Typically, the sodium addition and mixing period was 25-30 minutes. At the completion of the mixing period, the oxidizing gas was introduced to the calciner causing an exothermic reaction which was indicated by the internal thermocouples. As the reaction proceeded, the temperatures increased to the maximum then declined. This temperature decline usually occurred simultaneously with an increase in the oxygen concentration in the exhaust gas stream and it indicated the completion of the reaction.

Conversion to Oxide

The results of chemical analysis of samples from all the calciner experiments are listed in Table II. Conversion of sodium to oxide was >99% in most cases. Samples for free Na analyses were analyzed by one of two methods. One method utilized a distillation technique in which the sample was heated to $\approx 350^\circ\text{C}$ under a high vacuum. Any weight loss was noted and attributed to loss of sodium. In the second method, the sample was treated with methanol and the evolved gases were measured chromatographically.

The degree of conversion of sodium to the oxide was not influenced significantly by the oxidizing gas used nor the initiation temperature. The oxygen concentration in the exhaust gas was monitored to note the increase at the reaction end point. Terminating the reaction at the proper time based on this increase in oxygen concentration was found to be an effective method for consistently obtaining a high degree of conversion of sodium to oxide.

The free-sodium concentrations in the knock-out vessel were higher than in the calciner because some of the material in the knock-out vessel was collected during the early stages of the oxidation. At this point in the reaction, the fine material present in the calciner exhaust had a large fraction of unreacted sodium. A lower gas velocity in the calciner should reduce this particulate carry-over.

The sodium peroxide (Na_2O_2) concentration in the product appears to be influenced by the quantity of oxygen supplied to the calciner as indicated by the oxygen concentration in the exhaust gas. When the oxygen concentration in the exhaust gas is limited to ≤ 0.5 vol %, the sodium peroxide concentration in the product is minimized. An increase in this oxygen concentration resulted in increases in the Na_2O_2 content in the bed. Sodium peroxide reacts readily with sodium during subsequent additions. When the sodium peroxide inventory in the calciner bed becomes too large, an exothermic reaction occurs between the sodium peroxide and the sodium as it is delivered to and mixed with the bed. This type of reaction is indicated by the temperature increase shown in Fig. 4. The normal temperature profile during an experiment shows an initial temperature decline until flow of the oxidizing gas is started. In experiment 18, the temperature increased dramatically with the addition of sodium to the bed. When the Na- Na_2O_2 reaction was complete the temperature declined and the gas flow was started. The reaction then proceeded as usual. The problem with this type of temperature

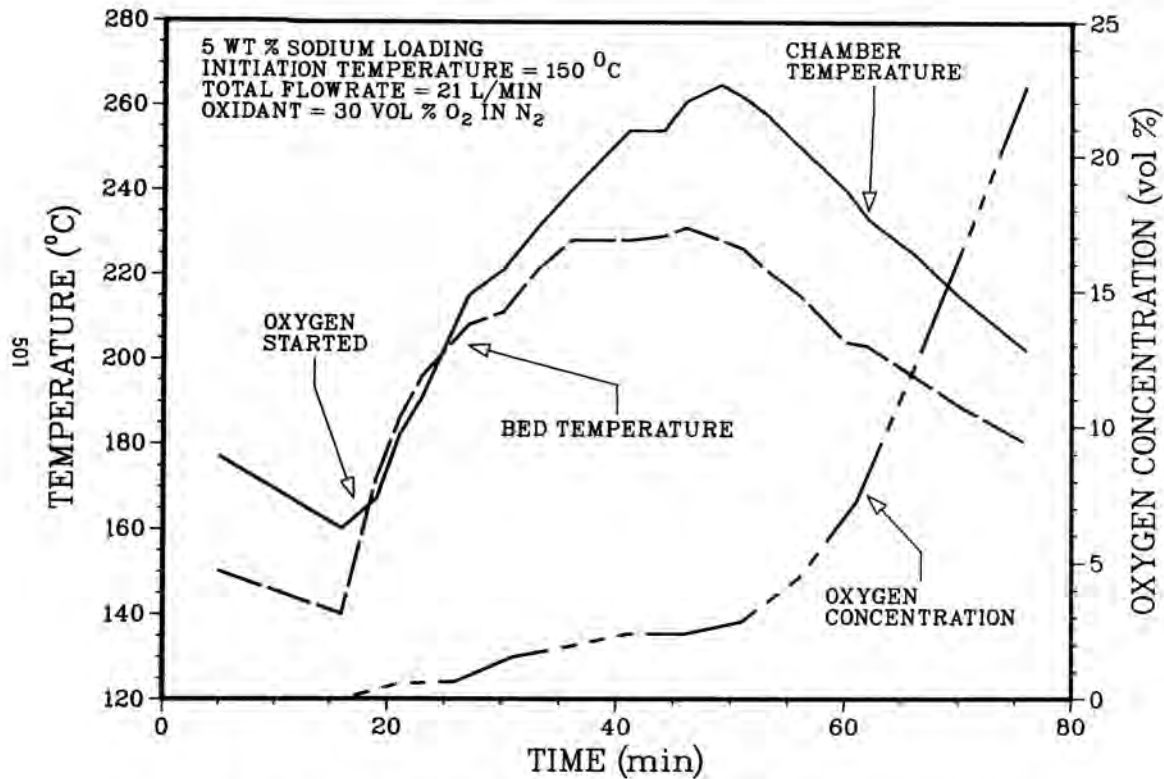


Fig. 2. Bed temperatures and oxygen concentration in the exhaust gas during Experiment 3.

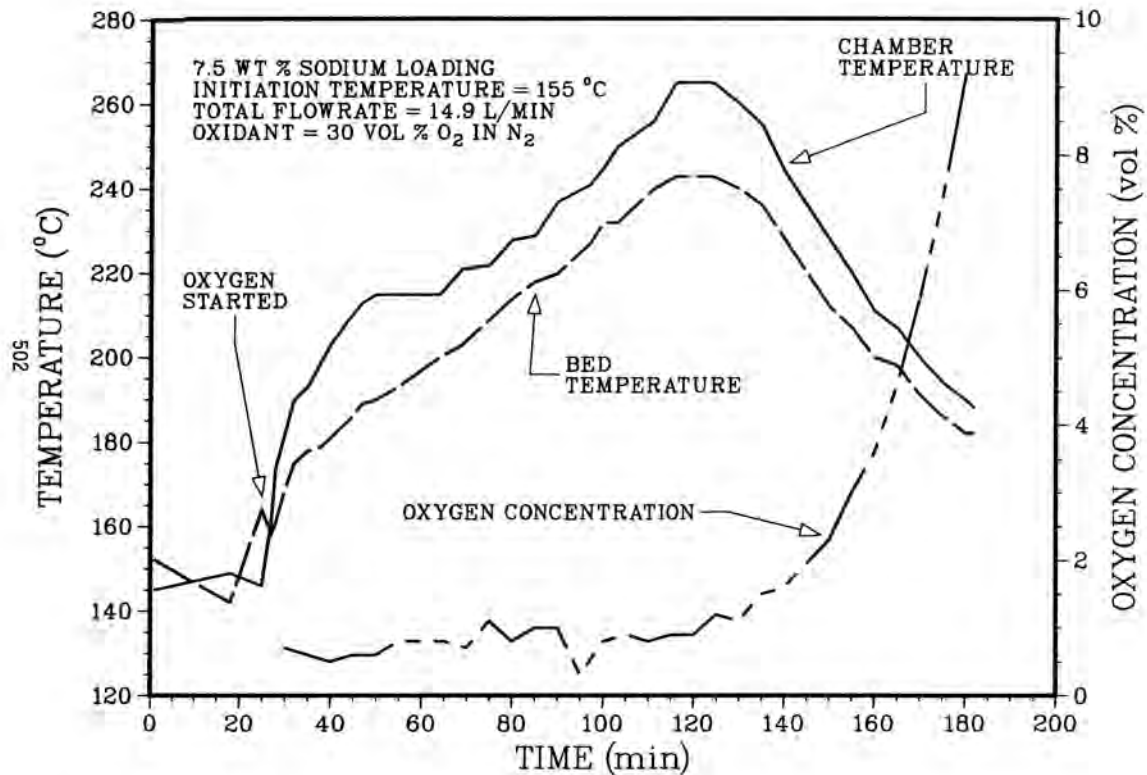


Fig. 3. Bed temperatures and oxygen concentration in the exhaust gas during Experiment 9.

Table II. Analytical Results

Experiment Number	Oxygen Concentration End-Point in Exhaust Gas (vol %)	Particulate Carry-Over (g/L) x10 ⁻²	Free Sodium Analysis (wt %)				Peroxide Concentration (wt %)			
			Sodium Inlet	Middle	Gas Inlet	Knock-Out Vessel	Sodium Inlet	Middle	Gas Inlet	Knock-Out Vessel
1*	25	4.06	---	---	---	---	---	---	---	---
2*	20	3.40	---	---	---	---	---	---	---	---
3*	23	4.90	---	---	---	---	---	---	---	---
4*	25	5.50	---	---	---	---	---	---	---	---
5	24	0.79	0.25	0.31	---	---	---	---	---	---
6*	24	5.10	---	---	---	---	---	---	---	---
7	28	3.60	0.89	---	0.12	---	12.1	---	12.75	---
8	20	3.71	0.03	0.03	0.05	---	14.0	13.3	12.2	---
9*	9	3.52	---	---	---	---	---	---	---	---
10	9	4.49	0.10	0.07	0.06	---	14.7	12.4	12.8	---
11*	2.25	5.97	---	---	---	---	---	---	---	---
12*	2	5.37	---	---	---	---	---	---	---	---
13*	2	9.40	0.03	0.07	0.24	0.58	7.82	8.24	9.11	---
14	2	16.30	---**	---**	0.02	6.9	7.72	7.68	7.17	6.55
15	2	5.90	0.05	0.27	0.04	---	8.82	9.77	8.49	7.64
16	2	5.10	0.46	0.01	0.22	0.13	10.12	9.30	9.29	6.87
17	0.8	3.50	0.19	0.08	0.06	30.0**	12.59	11.97	11.14	9.95
18	0.5	6.20	0.10	0.02	0.03	19.0**	10.51	10.04	9.53	6.97
19	1.5	5.04	0.06	1.1	1.2	27.0**	10.77	10.41	10.18	9.32
20	1.0	5.06	0.08	0.02	0.30	26.0**	11.21	9.55	7.59	7.13
21	0.8	7.74	---**	---**	---**	28.0**	11.0	11.7	8.31	11.8

* Subsequent additional made continuously-calciner always at elevated temperature.

** Analytical problems - not resolved.

RESULTS AND DISCUSSION

Operating Parameters

The operating conditions during each experiment are listed in Table I. Experimental parameters including sodium loading in the oxide bed, concentration of oxygen in the reaction gas, total gas flowrate, oxidation initiation temperature, and the end-point of the reaction as determined by the oxygen concentration in the exhaust-gas stream, were examined in these tests.

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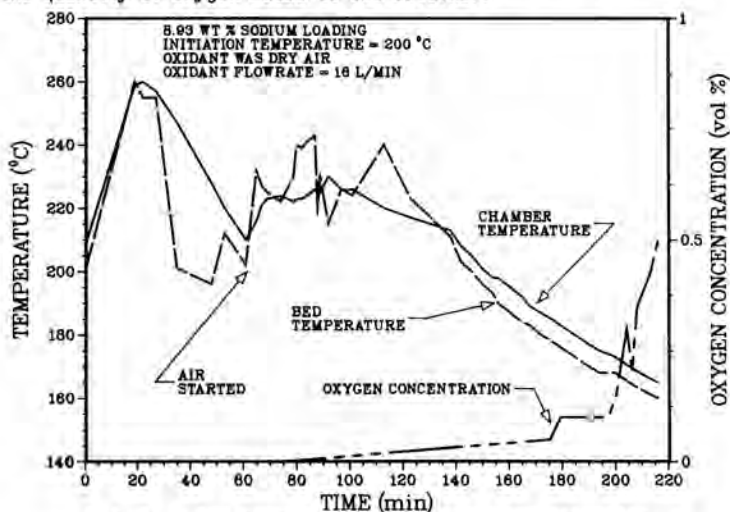


Fig. 4. Bed temperatures and oxygen concentration in the exhaust gas during Experiment 18.

Material Carry-over

The quantity of material retained in the particulate removal system was measured after each experiment, and these results are shown in Table II. The maximum acceptable amount of carry-over during these experiments was considered to be 0.1 g/L. This level was exceeded only once, during experiment 14, when the dry air flowrate was 17.9 L/min. In the majority of cases, the carry-over ranged between 0.03 and 0.06 g/L. The material carry-over can be reduced by increasing the diameter of the annulus between the Na inlet and gas exhaust tubes. In this equipment, the annular space

was small and the exit gas stream had a high velocity causing more particulate transfer. A larger annulus should reduce the quantity of particulate carryover.

Effect of Moisture

Two experiments (19 and 20) were performed to determine what effect a small amount of moisture in the oxidizing gas would have on the product. Experiment 19 utilized air with a relative humidity of 2% flowing at 16 L/min. The sodium loading on the oxide bed was 7 wt %. Experiment 20 utilized a 5 wt % sodium loading and 5% relative humidity air flowing at 16 L/min. The slightly moist air was expected to cause an increase in the size of the product particles by agglomeration of fines. Table III compares the particle size distribution in experiments 18, 19, and 20. Experiment 18 utilized dry air at a flowrate of 16 L/min and a 9 wt % sodium loading. The product from experiments 19 and 20 appeared, visually, to contain less fines and the particle size distribution results (Table III) support this observation. A larger particle size allows the product to be handled more easily and it appears that the addition of a small amount of moisture causes the size of the product particles to be larger. The disadvantage of moisture addition is that the hydrogen is retained as NaOH and this hydrogen (or moisture) could be released during the glass-melting process and cause operational difficulties.

Table III. Particle Size Distribution (wt %)

<u>Sieve No.</u>	<u>Experiment 18</u>	<u>Experiment 19</u>	<u>Experiment 20</u>
+14	15.01	18.40	13.57
-14, +20	7.50	7.22	6.02
-20, +25	3.65	3.14	2.61
-25, +60	23.16	39.27	35.63
-60, +100	27.83	22.35	26.87
-100	22.85	9.61	15.30

Reaction End-Point

The oxygen concentration in the exhaust gas from the calciner was monitored by sampling the gas and analyzing it with a gas chromatograph. The reaction end-point was judged to coincide with an increase in this oxygen concentration. The oxygen concentration that was used as the end-point indicator was varied from 0.5 to 25 vol %. The sodium peroxide content of the product varied with the oxygen concentration in the exhaust gas. The most desirable end-point indicator levels were in the 0.5-1.0 vol % range. The lowest sodium peroxide concentration noted in these experiments was

approximately 7 wt %. This level as well as concentrations up to 12 wt % caused no problems in operation of the system (Na + Na₂O₂ exothermic reaction). A minimum sodium peroxide inventory of 10 wt % will probably always result from the oxidation as performed in these experiments. Sodium-sodium peroxide reactions appear to become a problem only at sodium peroxide concentrations above 15 wt %.

Cesium Distribution

The final experiment in the series (21) examined the distribution of cesium in the calciner and the exhaust-gas system. Dry air at 16 L/min flowrate was used to oxidize a 6.5 wt % sodium charge. Non-radioactive cesium was added to the bed to achieve a starting concentration of 0.056 wt %. Table IV lists the cesium concentrations at various locations in the calciner and the gas-exhaust system after the experiment. A slight depletion of the Cs in the calciner was accompanied by an enrichment of the Cs concentration in the particulate removal system. Samples from filters placed at the gas vent indicated that 190 mg of Cs were deposited during the experiment. This quantity corresponds to 1.07% of the Cs inventory in the bed. This quantity of cesium should be easily handled with an efficient particulate removal and filtering system.

Table IV. Cesium Distribution

Dry air oxidizer, 16 L/min flowrate, 6.5 wt % sodium loading, starting Cs concentration in oxide bed = 0.056 wt %.

<u>Sampling Locations</u>	<u>Cesium Concentration (wt %)</u>	<u>Cs/Na wt Ratio, (ppm)</u>
Na Inlet	0.041	558
Middle	0.035	474
Gas Inlet	0.056	755
Knock-Out Vessel	0.083	1124
Cyclone	0.083	1119

CONCLUSIONS

The experimental efforts were designed to define conditions under which sodium waste can be efficiently and safely converted to sodium monoxide by oxidation in a calciner. Parameters that were studied included percent sodium loading on the oxide bed, oxygen concentration in the reaction gas, total gas flowrate, initiation temperatures, oxygen concentration in the exhaust-gas stream to indicate reaction end-point, humidity in the oxidizing gas, and behavior of cesium during oxidation.

Sodium loadings were varied from 5 to 9 wt %. Oxidations proceeded smoothly with no adverse effects noticed due to higher loadings. A loading of 10 wt % is suggested as a maximum.

The concentration of oxygen in the reaction gas should not exceed 50%. Higher concentrations cause high reaction temperatures producing a lack of process control and, apparently, finer particle size. Air as the sole source of oxygen is a feasible alternative; however, an oxidizer containing a higher oxygen concentration allows a shorter reaction time. A 30% oxygen concentration seemed optimum. Air may be used as the main oxygen source with supplemental oxygen added. Slightly moist air produced a coarser product which is desirable.

The amount of particulate carry-over is mainly determined by the gas flowrate. The maximum gas flowrate allowable is dependent upon the gas velocity at the exit. This can be varied by the geometry of the gas-exhaust system. If the gas velocity is low, the flowrate is determined by the reaction time desired. The total process cycle time was determined to be three hours with a 30 minute sodium addition/mixing period, a two-hour reaction time, and a 30 minute cool-down/unloading period prior to the subsequent sodium addition.

Process initiation temperatures ranging from 120 to 200°C were used successfully. The higher temperatures from 150 to 200°C are more desirable because a more uniform mixing of sodium and bed occurs in this temperature range. Above 200°C, the possibility of a Na-Na₂O₂ reaction increases.

Excess oxygen generates higher Na₂O₂ concentrations in the product. The Na₂O₂ may react with subsequent sodium additions. An oxygen concentration of 0.5 to 1.0% in the gas-exhaust stream indicates completion of the reaction while limiting the quantity of Na₂O₂ generated to <10 wt %.

Most of the cesium in the sodium charge remained in the oxide bed, and only a slight enrichment of cesium was observed in the particulate removal system. Approximately 1% of the cesium was carried out of the calciner.

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