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Journal of Solid State Chemistry 177 (2004) 3460–3468

JOURNAL OF SOLID STATE CHEMISTRY

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A novel method of non-violent dissolution of sodium metal in a concentrated aqueous solution of Epsom salt

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Abstract

A new technique of non-violent and fast dissolution of sodium metal in a concentrated aqueous solution of Epsom salt ($MgSO_4.7H_2O$) at room temperature (RT) has been developed. The dissolution process is mildly exothermic but could be carried out even in a glass beaker in air under swift stirring condition. The reaction products consist of mixed salts of $MgSO_4$ and Na_2SO_4 as well as $Mg(OH)_2$ which are only mildly alkaline and hence are non-corrosive and non-hazardous unlike NaOH. A 50 mL solution having Epsom salt concentration of 2 M was found to give the optimal composition for disposal of 1 g of sodium. Supersaturated (>2.7 M), as well as dilute (<1.1 M) solutions, however, cause violent reactions and hence should be avoided. Repeated sodium dissolution in Epsom solution produced a solid waste of 4.7 g per g of sodium dissolved which is comparable with the waste (4 g) produced in 8 M NaOH solution. A 1.4 M Epsom solution sprayed with a high-pressure jet cleaner at RT in air easily removed the sodium blocked inside a metal pipe made of mild steel. The above jet also dissolved peacefully residual sodium collected on the metal tray after a sodium fire experiment. No sodium fire or explosion was observed during this campaign. The Epsom solution spray effectively neutralized the minor quantity of sodium aerosol produced during this campaign. This novel technique would hence be quite useful for draining sodium from fast breeder reactor components and bulk processing of sodium as well as for sodium fire fighting.

Keywords: Sodium disposal; Epsom salt; Aqueous solution; pH control; Sodium cleanup; Sodium fire fighting; Fast breeder reactors

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1. Introduction

In fast breeder reactor (FBR), alkali metals such as sodium serve as heat transfer media in cooling circuits which transfer thermal energy to heat water or to produce steam. In the course of their operation, need arises for draining sodium from reactor components, bulk processing of unwanted/leaked sodium and for the removal of sodium from sodium bonded spent fuels, fast auxiliary systems such as cold traps, filters, relief valves, etc. There are several techniques presently used mostly under inert conditions for sodium removal and disposal, notable among them being dissolution in NaOH aqueous solution or ethanol, water vapor-nitrogen process, water vacuum process, cold steam process or vacuum distillation. However, each technique is known to have its limitations. Especially, the reaction of sodium with water invoke exothermic and violent chemical reactions. Furthermore, the reaction products are highly corrosive. Hence there is a search for improved methods.

When heated in dry air, sodium melts at 97.8°C and ignites. A mixture of dense and highly corrosive sodium monoxide (Na_2O) and peroxide (Na_2O_2) fumes is formed by the reaction of sodium with air or oxygen. Sodium reacts rapidly with water to give NaOH and hydrogen:

$$Na + H_2O \rightarrow NaOH + 1/2H_2 - 35.2\,\text{kcal/mol}. \qquad (1)$$

Sufficient heat is liberated by this reaction to melt the sodium and frequently ignites the evolved hydrogen if air is present. In an accident of sodium cooled FBR, sodium fire following the leakage of the primary coolant can disperse a large quantity of sodium oxide aerosol containing radioactive ^{24}Na and fission products [1]. Effective ways of neutralizing such aerosols are very

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doi:10.1016/j.jssc.2004.05.030

much needed for the safety of reactor operators as well as for the public.

In the past, sodium has been disposed off by igniting it by a fine spray of water and allowing it to burn in a disposal yard located at a remote place while the residues were dissolved with a fine spray of water and the NaOH accumulated neutralized separately [2]. However, such a burning process releases highly corrosive sodium aerosols into atmosphere. Use of heavy alcohol like ethyl carbitol is not recommended for sodium cleanup since explosions in Rapsodie, France in 1994 and in FZK research facility in Germany in 1996 during such a campaign indicated that it could decompose to give gaseous products under some conditions [3,4]. The caustic process which uses a 10 M NaOH activated aqueous solution is presently used for destroying large quantities of sodium while decommissioning the FBRs [5]. In this process also sodium reacts with water but the reaction is made non-violent due to the presence of concentrated NaOH. However, to ward off any explosion risk due to hydrogen, only small quantities of molten sodium are injected on line at a given time into a strong current of NaOH solution. The aqueous NaOH content is continuously adjusted to 10 M while the hydrogen gas is diluted with nitrogen (acting as a purge gas) and then released via a stack. The FBRs in Dounreay, UK also employ a similar process using a 15 M aqueous solution of sodium and potassium hydroxide for the disposal of NaK alloy coolant [6]. The NaK feed rate was a maximum of 18 kg/h while the solution temperature was kept below 85°C. However, such a caustic process is not suitable for cleanup of sodium in reusable reactor components as NaOH and KOH are highly corrosive.

Sodium-bonded spent nuclear fuel is distinguished from other nuclear reactor spent fuel by the presence of metallic sodium which is a highly chemically reactive material. When the driver fuel, used mainly in the center of the reactor core to 'drive' and sustain the fission chain reaction, is irradiated for long duration, the metallic fuel swells as fission products are generated until it reaches the cladding wall. During this process, some metallic sodium enters the metallic fuel and becomes inseparable from it due to inter diffusion between the fuel and cladding. Therefore, mechanical stripping of the driver spent nuclear fuel cladding is not a practical means of removing sodium. After careful consideration of various options, US DOE has decided to treat electro metallurgically the EBR-II spent nuclear fuel (about 25 metric tons of heavy metal) [7].

In this work, in order to arrive at a non-violent and eco-friendly method of sodium disposal, a number of aqueous salt solutions were tried for sodium dissolution. Literature [8] reports suggest that alkaline earth metal sulfates are reduced to the sulfides by sodium, i.e.,

$$BaSO_4 + 2Na \rightarrow BaS + Na_2O_2 + O_2. \tag{2}$$

Experiments with water insoluble salts such as gypsum, i.e $CaSO_4 \cdot 2H_2O$ did really confirm that sodium dissolution in them is not feasible. Addition of sodium into a mixture of gypsum and water resulted in sodium fire accompanied with aerosol release. However, the situation changed drastically with water soluble salts. Among those tried, an aqueous solution of $(NH_4)_2SO_4$ was found to dissolve sodium efficiently resulting in the formation of Na_2SO_4. However, a drawback in this case is the intense release of ammonia gas which is not desirable since sodium is known to react violently with ammonia. Sodium dissolution in aqueous solutions of salts like $Zn(NO_3)_2$ and $CuCl_2$ whose host metals do not react with water turned very violent at all salt concentrations. Other salt solutions studied include NaCl, Na_2SO_4, KCl, LiCl, $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 2H_2O$, $CdCl_2 \cdot 2.5H_2O$, and $BaBr_2 \cdot 2H_2O$. Preliminary studies showed that the dissolution process is not entirely peaceful in aqueous solutions of KCl, NaCl and $BaBr_2$. However, $CdCl_2 \cdot 2.5H_2O$ was quite effective. On sodium dissolution, a black precipitate characteristic of CdO was observed. $CaCl_2 \cdot 2H_2O$ aqueous solution which gave rise to $Ca(OH)_2$ precipitate was also found to be effective. Na_2SO_4 is another salt in which the dissolution was found to be peaceful at high salt concentrations. However, in this solution, Na_2SO_4 precipitation occurred during sodium dissolution due to common ion effect. Moreover, the reaction product consists of NaOH whose alkalinity is high. Despite $Mg(OH)_2$ precipitation, $MgCl_2$ was not as effective as $MgSO_4$. Among the aqueous salt solutions studied, Epsom ($MgSO_4 \cdot 7H_2O$) was found to be very efficient for non-violent dissolution of sodium metal which results in non-corrosive reaction products. It is also an inexpensive (50 US $ per metric ton) and eco-friendly (used as a fertilizer) salt. Moreover, the formation of $Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$ mineral (natural bloedite) is known to occur in nature and the solubility of Epsom in water is quite high (91 g/100 cm^3 at 40°C) [9]. Hence detailed studies were carried out only with Epsom salt solution.

The objectives of this work are two-fold. First is the development of an improved method of non-violent dissolution of sodium metal in which the reaction products are non-corrosive and non-hazardous unlike that of caustic process employing NaOH so that the same process could be used for large scale sodium processing as well as for the cleanup of FBR components. Second is to develop an inexpensive liquid hydrant/spray which is effective for sodium fire fighting and sodium aerosol neutralization since such a development would provide a valuable tool in the utility and safety of sodium cooled FBRs.

2. Experimental

A major complication in sodium disposal is the low density of sodium ($d = 0.97$) because of which it has a tendency to float in liquids and once in contact with air, it burns readily to form dense oxide fumes. But this difficulty was overcome with vigorous stirring of the solution. The centrifugal force provided by stirring prevents the sodium from floating. Once sodium metal is dropped into the Epsom solution under stirring, it reacts with water quickly and melts. The molten sodium readily wets efficiently and reacts fast with the Epsom salt solution [10]. Sodium dissolution was generally carried out in a fume hood. A series of experiments with different concentrations of Epsom salt revealed that in a concentrated (but slightly under-saturated) aqueous solution of Epsom salt, sodium dissolves peacefully without any violent reactions even at room temperature in air. Both high pure (Ranbaxy make, Laboratory reagent) as well as fertilizer grade Epsom salts were used. The rise in solution temperature was continuously monitored with the help of a chromel–alumel thermocouple wire inserted into the solution. An X–Y recorder was used to plot the temperature of the solution as a function of time since the sodium drop. The recorder chart speed was kept at 10 cm/min (X-axis) while the ordinate showed the temperature measured by the thermocouple (4.1°C/cm). The alkalinity of the solution before and after the sodium dissolution was measured with the help of a pH meter. The effects of water content, salt content, quantity of solution as well as the quantity of sodium on the solution temperature were studied. To reduce solid waste, the effect of repeated dissolution of sodium on the same solution was also studied. However when the mass of sodium was higher than 5 g, additional air ventilation was found essential to dilute the hydrogen concentration and to prevent the fire. A comparison of the above Epsom process with the caustic process has been made under identical experimental conditions. In order to remove the sodium blocked inside a metal pipe as well as to dispose of partially burnt sodium (~30 kg) left out on a metal tray, a portable high pressure (140 bar) cold water jet cleaner machine (actually a car washer machine) having a flow rate of 520 L/h was used to spray the Epsom solution.

Table 1
Powder XRD data of water insoluble salt and that of $Mg(OH)_2$ reported in JCPDS-file

S. no.	*d*-Value (A)	Rel. int (%)	$Mg(OH)_2$			
			Exptl [11]		Calculated [12]	
			d(A)	Rel. int	*d*(A)	Rel. int.
1	4.7576	58.4	4.785	53	4.7400	83.7
2	4.5177	31.6				
3	4.3852	25.7				
4	4.3323	16.2				
5	4.1617	19.4				
6	3.9865	32.5				
7	3.5971	12.4				
8	3.4013	12.5				
9	3.2667	12.3				
10	2.9834	14.0				
11	2.9261	12.8				
12	2.7925	14.4				
13	2.7183	16.5	2.6292	13.7		
14	2.5887	14.7				
15	2.4232	13.2				
16	2.3619	100.0	2.367	100	2.3615	99.9
17	2.0736	5.8				
18	1.9391	5.3				
19	1.7939	30.7	1.7963	29	1.7878	42.5
20	1.5716	30.7	1.5723	33	1.5725	25.1
21	1.4946	10.7	1.4931	13	1.4925	12.2
22	1.3733	7.6			1.3666	12.0
23	1.3092	8.2			1.3088	8.0

The present results as well as the literature data (experimental as well as theoretical) were all obtained with Cu$K\alpha_1$ X-rays.

3. Results and discussion

3.1. *Reaction products*

A solution having Epsom salt and water to Na weight ratios of 25 and 33, respectively (~2 M) was found to give the optimal composition for sodium disposal. This will be referred to as standard solution. But the sodium dissolution was found to proceed peacefully in the solute concentration range 1.4–2.4 M as long as the Epsom salt to Na weight ratio is $\geqslant 25$. Litmus test confirmed that the vapor released during dissolution is neither acidic nor basic indicating the absence of sodium aerosol release. Gas monitors have, however, confirmed the release of hydrogen during dissolution. After the completion of sodium dissolution, the water insoluble salt was separated by filtering the solution and drying the filtered residue under an infra-red lamp. The remaining solution was dried at 100°C in a hot plate so that the soluble salts could be recovered and weighed. When viewed through optical transmission microscope, both the powder samples were found to be well grown transparent crystals (37–210 μm) but the dissolved salts were relatively smaller in size than that of the insoluble salts. Litmus test revealed that the water insoluble salt is alkaline. Powder X-ray diffraction (XRD) data in Table 1 confirmed that the water insoluble salt (15% by weight) is indeed $Mg(OH)_2$. The dissolved salts (85% by weight) were found to be complex but indicative of the mixed salts of Na_2SO_4 and $MgSO_4$. Interestingly, no X-ray diffraction lines corresponding to NaOH was seen in it. In any case, any NaOH formed due to $Na–H_2O$ reaction would be readily converted to $Mg(OH)_2$ due to the following reaction:

$$2NaOH + MgSO_4 \rightarrow Mg(OH)_2 + Na_2SO_4. \tag{3}$$

3.2. *Quantity of sodium*

Since the Epsom technique is proposed to be scaled up to dissolve larger quantities of sodium, the rise in temperature of the standard solution during sodium dissolution as a function of increasing sodium mass was studied. The solution quantity was increased (from 131 to 957 mL) in proportion to the mass of sodium (2.78–20 g) dissolved. Results (Figs. 1a–c) show that the maximum temperature is attained in about 10 s irrespective of the sodium mass indicating that sodium dissolution rate is swift in all cases. While 2.78 g of sodium increases the solution temperature by 30°C, a seven-fold increase in sodium, i.e, 20 g sodium dissolution increases the solution temperature only by 38°C. The rise in solution temperature does not depend critically on sodium quantity since the total quantity of solution used for sodium disposal also increased proportionately. However, for large quantities of sodium processing inert gas purging will be essential to dilute the hydrogen gas released during dissolution.

3.3. *Quantity of solution*

The dependence of rise in solution temperature during sodium dissolution on the total quantity of solution (Epsom salt + H_2O) was studied. While the water to salt weight ratio was kept same at 1.32, the water to sodium ratio was increased four-fold from 16.52 to 66.07. The total quantity of solution also increased four-fold, i.e., from 62 to 236 mL. The quantity of sodium added was kept nearly same, i.e., 2.48–2.67 g when the total quantity of solution increased. The rise in solution temperature decreased from 58°C to 17°C, as expected since for a constant sodium mass, the energy released during sodium dissolution remain same, while the quantity of solution to be heated increased. The time taken to attain the maximum temperature decreased gradually from about 9 to 5 s when the solution quantity decreased from 236 to 62 mL. However, in the latter case intense fire resulted due to the ignition of hydrogen released at high solution temperature. Epsom salt to Na ratio and water to Na ratio in this mixture were 12.5 and 16.5, respectively. The recommended ratios for safe sodium disposal as those are, however, 25 and 33, respectively.

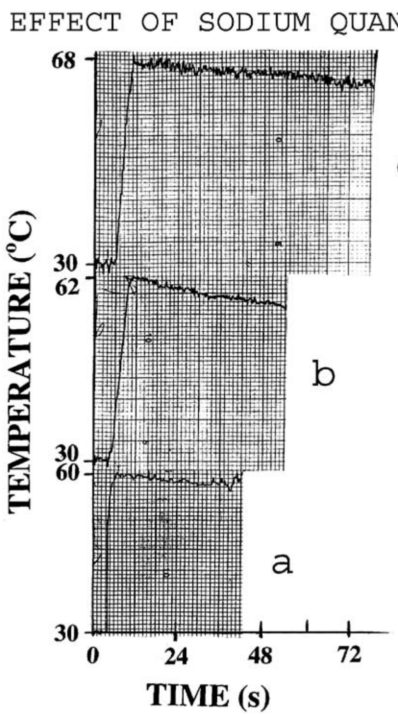

Fig. 1. The dependence of solution temperature versus time since the addition of sodium on the quantity of sodium dissolved. Sodium, Epsom and water weights, respectively in grams: 2.78, 69.58, 91.84 (a), 9.25, 231, 305 (b) and 19.99, 500, 660 (c). The molarity of the solutions (M) are: 2.15 (a), 2.1 (b) and 2.1 (c).

3.4. *Epsom salt content*

The effect of Epsom salt content in the aqueous solution used for sodium dissolution was studied by increasing the salt concentration from 1.1 to 2.7 M, while the sodium and water content were kept more or less the same. Table 2 shows that the dissolution slows down a bit with increasing solution volume while the time taken to reach maximum temperature increases systematically from about 7 to 14 s as the mass of the salt increased for nearly constant water quantity. The rise in solution temperature reduces from 26°C to 19°C with increase in solution volume. However, the dilute salt solution gives rise to hydrogen fire despite a moderate temperature rise (26°C). When the solute concentrations (1.43 and 1.95 M) were within the limits recommended for safe sodium disposal, the sodium dissolution has proceeded peacefully without any fire. The dissolution slowed down a bit in a slightly supersaturated solution (2.37 M). However, in a highly supersaturated salt solution (2.72 M) in the absence of sufficient quantity of water, sodium dissolution in Epsom salt was found to be incomplete which resulted in fire and smoke from the un-dissolved sodium on exposure to air. Similarly, in highly dilute Epsom solutions (<1 M), sodium-water reaction turned violent which should hence be avoided.

3.5. *Water content*

The effect of water content in the salt solution used for sodium dissolution was studied by keeping the quantity of sodium and Epsom salt nearly constant while the water quantity was increased from 89.2 to 168.8 g. The salt concentrations used in this study were 2.13, 1.57 and 1.25 M of solution. Figs. 2a–c show that

Table 2
The effect of Epsom salt content in the aqueous solution used for sodium dissolution on the rise in solution temperature as a function of salt concentration from 1.1 to 2.7 M, while the sodium (~2.6 g) and water content (~150 mL) were kept more or less the same

S. no.	Salt content (g)	Solution quantity (mL)	Molarity (M)	Time taken to reach maximum temperature (s)	Rise in temperature (°C)
1	47.00	174	1.09	7	26
2	99.30	207	1.95	9	23
3	133.10	228	2.37	12	20
4	178.30	266	2.72	14	19

the rise in temperature is more with decreasing water content because of the decrease in the total quantity of solution from 207 (Fig. 2c) to 129 ml (Fig. 2a). With decreasing water content, the time taken to attain the maximum temperature decreased little, from about 8 (Fig. 2c) to 5 s (Fig. 2a). The sodium dissolution is, however, fast and peaceful in all the three cases which indicate the presence of sufficient quantity of Epsom salt and water.

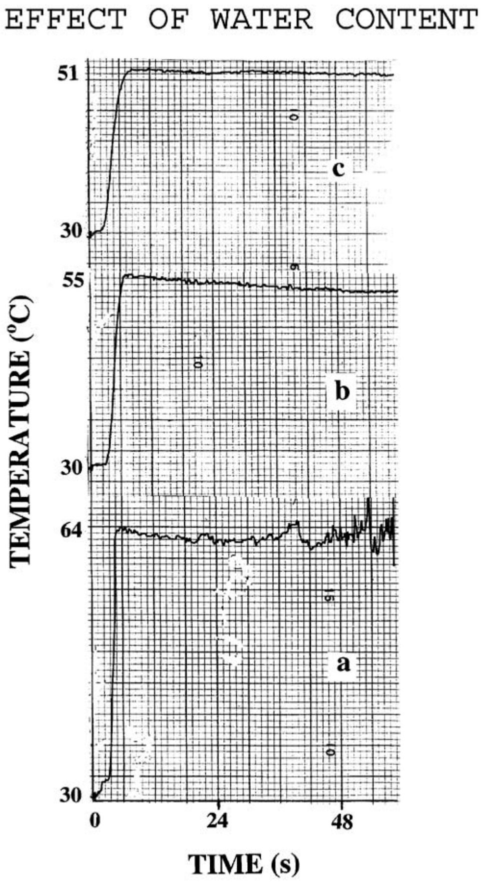

Fig. 2. The dependence of solution temperature versus time since the addition of sodium on the water content in Epsom solution. Sodium, Epsom and water weights, respectively in grams: 2.70, 67.6, 89.2 (a), 2.53, 63.3, 126.5 (b) and 2.56, 64, 168.8 (c). The molarity of the solutions (M) are: 2.13 (a), 1.57 (b) and 1.25 (c).

3.6. Dissolution in aqueous NaOH solution—a comparison

Figs. 3a–c deal with the effect of water content in the NaOH salt solution on the sodium dissolution rate and rise in temperature. The NaOH salt to sodium ratios were kept constant at 25 while the water content was increased more than two-fold, i.e., from 85.13 to 183 mL. This corresponds to a solution concentration range of 14–8 M, respectively. Due to the relatively low molecular weight of NaOH (40) in comparison to Epsom (246.47), the molar concentrations of the solute in NaOH solution are nearly an order of magnitude higher than those used in the Epsom solution. In general, the quantity of NaOH produced from sodium-water reaction, via Eq. (1) is negligible when compared to the NaOH present already in the solution. For example, in Fig. 3a, the latter is 14.4 times larger than the former. Figs. 3a–c show that the rate of sodium dissolution in the NaOH process decreases drastically with decreasing water content since the water that is available for reacting with sodium is not only relatively less but it is also surrounded by more OH^- ions. However, the rise in solution temperature (19–21°C) is more or less independent of water content since the sodium dissolution rate decreases drastically with decreasing water content and hence the energy due to sodium-water exothermic reaction is released relatively slowly when water content is less. Therefore, the time taken to heat the solution to its maximum temperature increases drastically with decreasing water content (from 8 to 80 s as one goes from Figs. 3a–c) which increases heat dissipation losses. Thus the maximum temperature reached in Fig. 3a is less than what is expected with decreased solution quantity. In contrast, in the Epsom solution, as seen earlier in Fig. 2, the sodium dissolution proceeds fast irrespective of the solute concentration. In fact unlike the case with NaOH when the quantity of Epsom solution is relatively less, i.e., with decreasing water content the sodium dissolution rate proceeds a little fast and hence the time taken to reach the maximum temperature is reduced (8–6 s) while the rise in temperature is relatively high.

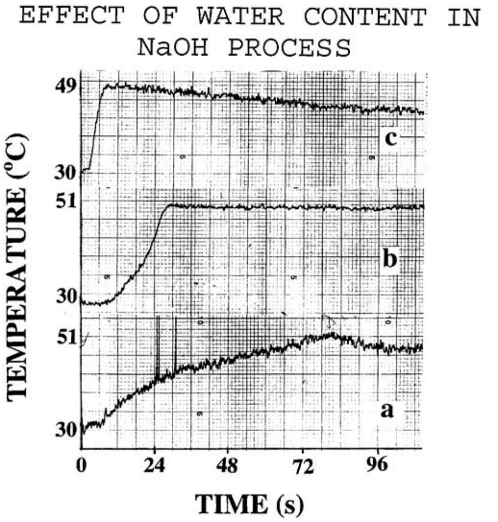

Fig. 3. The dependence of solution temperature versus time since the addition of sodium on the water content in NaOH solution. Na, NaOH and water weights, respectively in grams: 2.58, 64.49, 85.13 (a), 2.88, 72.16, 144.3 (b) and 2.77, 69.32, 183 (c). The molarity of the solutions (M) are: 14 (a), 10.1 (b) and 8.1 (c).

Sodium is a highly reactive metal. On exposure to moist air, a film of sodium monoxide (Na_2O) is formed around it, which reacts first with water exothermically to produce NaOH. In pure water, sodium was found to explode within 3 s which indicates that the Na_2O outer layer is removed instantly in pure water under stirring condition whereas in NaOH solution it is possibly getting removed slowly. However, even with pure sodium metal obtained after the removal of the sodium oxide surface layer, the dissolution was found to proceed relatively slowly in concentrated (14 M) sodium hydroxide solution when compared to 8 M solution. This confirms that the major reason for slowing down of sodium-water reaction in 14 M solution is the presence of excess of Na^+ and OH^- ions which form a sort of envelop around the water molecules since they are highly polar. In fact, studies with different salt solutions have shown that the slowing down of the sodium dissolution rate with increased salt content is observed only in the case of NaOH and possibly in KOH solutions. It is one parameter which is indicative of the free ion character of these two salt solutions which distinguishes them from nearly all other salt solutions.

A comparison of Figs. 2 and 3 indicate that for sodium dissolution carried out under nearly identical conditions, the rise in temperature in the Epsom process (34°C, 25°C or 21°C) is slightly higher than those obtained in NaOH process (21°C, 21°C or 19°C). This again is a consequence of the difference in reaction rate in the two processes. When the sodium dissolution proceeds fast in both dissolution processes, e.g., Figs. 2c and 3c, the difference in rise in temperature observed in the two processes is minimal (21°C and 19°C, respectively).

3.7. *Sodium solubility limits in Epsom and NaOH solutions*

In Epsom solution, for a given water content (~ 100 mL), the amount of sodium that could be dissolved peacefully increased from 6 to 10.5 g when the salt content was increased from 1.4 to 1.9 M. The above solubility limits were arrived at on the basis of observation of sodium fire initiated by sodium-air reaction when further sodium was added. In contrast in the NaOH solution, for a given water content (~ 120 mL), the sodium solubility has been found to decrease from about 30 to 15 g when the salt content was increased from 8 to 12 M as expected from the reduced availability as well as reduced thermodynamic activity of water at such high salt concentrations. The sodium solubility limit in this case was arrived at on the basis of NaOH salt reaching its solubility limit in water, i.e., further sodium addition resulted in NaOH precipitation. Another notable difference between the two processes is seen in their super-saturated solutions. While sodium addition in super-saturated Epsom solution results in sodium fire and aerosol release, super-saturated NaOH solution was found to dissolve sodium peacefully though very slowly.

3.8. *Repeated addition of sodium and production of solid waste*

For radioactive sodium disposal, it is necessary to reduce the quantity of waste generated. This means it is necessary to find ways to reduce the presently used Epsom salt solution quantity per unit quantity of sodium dissolved (~ 50 mL/g). However, we have seen earlier that since the dissolution process is quite fast, a reduction in the quantity of Epsom solution by 50% boosts the rise in temperature nearly by a factor of 2 (i.e., 29–58°C) which results in the ignition of hydrogen in air. A way to overcome this problem is to add sodium repeatedly in the standard Epsom salt solution so that the rise in solution temperature is within a limit. After each dissolution, the beaker containing the standard solution was cooled to RT quickly by immersing it in an ice bath before the commencement of the next dissolution. The standard Epsom solution produced a solid waste of about 7.8 g/g of sodium dissolved. This figure was obtained by dissolving sodium repeatedly 7 times in the same solution and evaporating the water. Eighth addition resulted in sodium fire thereby indicating that the safe solubility limit has been crossed. The decreased molarity of Epsom solution on sodium dissolution as a result of the conversion of $MgSO_4$ to $Mg(OH)_2$ and Na_2SO_4 is responsible for the above solubility limit.

In 2 M Epsom solution, the stirrer speed had to be increased on repeated sodium dissolution due to the increased viscosity of the solution as a result of the formation of $Mg(OH)_2$ which is milky in nature. This difficulty was overcome by employing a larger quantity of dilute Epsom solution. For example 700 mL of 1.2 M solution produced the same solid waste per unit weight of sodium dissolved as 160 mL of 2 M Epsom solution. However, the viscosity of the dilute solution did not pose a problem during repeated sodium dissolution. Re-conversion of $Mg(OH)_2$ product obtained after sodium dissolution to $MgSO_4$ using a little amount of H_2SO_4 (3 mL/4 g of sodium) pushed up the sodium solubility limit by at least 50% which brings down the solid waste produced to 4.7 g per 1 g of sodium dissolved. In 8 M of NaOH solution, sodium was dissolved similarly. The solid waste produced in this case was 4 g of NaOH/1 g of Na which compares reasonably well with the figure obtained with Epsom process. Stirring speed was not found to be critical in this case as the solution viscosity did not increase significantly unlike that in Epsom solution. Therefore from radioactive solid waste considerations, the two processes are comparable. However, NaOH has to be converted to NaCl or Na_2CO_3 before storage/disposal while in the Epsom process the waste could be stored/disposed off directly. So Epsom process could be a favorable option in the disposal of radioactive as well as non-radioactive sodium.

3.9. Preliminary studies on sodium cleanup and sodium disposal

Unlike the disposal studies discussed above, the cleanup experiments are more delicate and ideal conditions such as stirring are not feasible. For example, in one case study of sodium removal from irradiated core sub-assemblies, ethanol was pumped from one tank into another tank through the core-assembly using compressed nitrogen during which the ethanol cleans only the outer surface of the sub-assembly since sodium reacts only gently with alcohol, liberating hydrogen through the following reaction:

$$2Na + 2C_2H_5OH \rightarrow 2C_2H_5ONa + H_2. \tag{4}$$

For each such cycle it took about 15 min and a total of 5–6 cycles of cleaning were found essential to remove the sodium completely. In one such experiment, about 80 L of ethanol was used to remove about 100 g of sodium from the sub-assembly. When compared to this, the Epsom salt solution needed for 100 g of sodium dissolution (5 L) is quite less. For sodium removal from fuel sub-assembly, a similar cleaning procedure has been followed as steam cleaning could not be adopted since the fuel was pyrophoric in nature. At the end of the process, all sodium and sodium hydroxide were removed leaving behind oxides and other impurities which could be removed only with subsequent steps of reaction with steam and washing with water [13]. But for active and large components this process has been reported to give rise to problems of inflammability of alcohol and the issue of organic active waste management. Another process used for sodium cleaning is steam or dispersed water in inert gas (nitrogen or CO_2). While nitrogen gas involves a risk of caustic corrosion, CO_2 transforms NaOH into a non-corrosive carbonate, which can also limit the efficiency and may stop the reaction by creating a protective layer of carbonate between the sodium and water [14].

The real advantage of the Epsom process, namely the pH control would be fully realized in sodium cleanup. This process could easily replace the presently used organic cleaning. When the standard Epsom salt solution was poured into a 3-necked cylindrical glass flask containing 2 g of sodium in air, fire and smoke were generated due to floating sodium coming in contact with air. However, when the experiment was repeated with argon purge gas, the sodium got dissolved peacefully without fire or smoke in about 3 min, the time taken to pour the solution into the flask. The quantity of Epsom salt solution needed for sodium dissolution used in this case was approximately twice that used in sodium disposal described earlier. Argon purging causes the solution to bump which is akin to the rotation process adopted for sodium dissolution and hence the sodium dissolved swiftly. $Mg(OH)_2$ and MgO suspensions could be dissolved easily with 0.1 N HNO_3. Therefore, subsequent to sodium cleaning, washing with water/steam and then with 0.1 N HNO_3 are recommended for removing any undissolved salts sticking with reactor components. As the above preliminary result is highly encouraging, it is proposed to repeat this experiment simulating the actual cleanup situations described above. The salient features of the NaOH and Epsom processes are summarized in Table 3.

A 1.3 M Epsom solution sprayed with a high-pressure jet cleaner at RT in air in a open yard easily removed the sodium ($\sim$1 kg) blocked inside a mild steel metal pipe (length $\sim$24$''$ and diameter $\sim$2$''$) in 5 min. In this campaign, a dilute solution (1.3 M) was found to be more effective than the standard (2 M) solution for sodium dissolution and its removal as well as for containing the sodium aerosol release. Interestingly, the above sodium blockage could not be removed despite prolonged heating with an oxy-acetylene torch accompanied by repeated hammering since sodium probably formed inter-metallic compounds with mild steel. The solution when sprayed at a 45° inclination was found to be effective in sodium removal as it provided an easy pathway for the hydrogen released. When the solution was sprayed directly into the pipe, the hydrogen trapped inside could not find an easy pathway. As a result, the hydrogen gas pressure has built-up inside the pipe and after a while the entire quantity of sodium trapped inside the metal pipe was thrown out suddenly which resulted in hydrogen ignition as well as sodium aerosol release since a large quantity of molten sodium suddenly came in contact with the atmosphere which was beyond the capacity to cope-up with a single solution jet. However, the above solution jet dissolved peacefully residual sodium (~ 50 kg) collected on a metal tray after a sodium fire experiment within a few minutes. The solution spray effectively acted as an efficient neutralizing agent to the sodium aerosol produced during this operation. This novel technique would hence be quite useful for draining sodium from sodium metal cooled fast breeder reactor components, bulk processing of sodium as well as for sodium fire fighting. The only precaution to be taken in this campaign in a closed environment such as reactor containment building is to provide a pathway for the hydrogen released during sodium dissolution. This could be easily achieved by controlling the solution spraying rate as well as by providing sufficient ventilation to reduce the hydrogen concentration in air. In the high-pressure car washing jet used in this experiment, the air accompanying the solution jet effectively diluted the hydrogen released during sodium dissolution thereby preventing hydrogen ignition or explosion.

Table 3
A summary of the salient features of NaOH and Epsom processes used for sodium dissolution

Sl. no.	Property	NaOH	Epsom
1	Concentration of the solution for non-violent sodium dissolution	8–15 M	1–2 M
2	Dissolution in supersaturated solution	Slow dissolution	Violent reaction
3	Dissolution condition	Stirring	Stirring
4	Reaction products	Corrosive NaOH	Less corrosive $Mg(OH)_2$, Na_2SO_4 (pH 8–10)
5	Nature of reaction	Exothermic	Exothermic
6	Hydrogen release	Yes	Yes
7	Sodium solubility limit	~ 30 g/100 mL[a] (decreases with molarity)	~ 10 g/100 mL[b] (increases with molarity)
8	On repeated sodium dissolution	Molarity increases due to the production of NaOH	Molarity decreases due to the conversion of $MgSO_4$ to $Mg(OH)_2$ and Na_2SO_4
9	Sodium dissolution rate	Slowing down above 10 M	More or less same at 1–2 M
10	Solid waste generated per gram of Na after evaporation	4 g (for 8 M solution)	7.8 g (for 2 M solution) or 4.7 g after converting $Mg(OH)_2$ to $MgSO_4$
11	Waste disposal	NaOH to be converted to NaCl or Na_2CO_3	Can be stored or disposed off as it is
12	Utility	Sodium processing	Sodium processing, FBR components cleaning and sodium fire fighting

[a] Limitation is due to the NaOH precipitation.

[b] Limitation is due to the onset of sodium fire.

4. Conclusions

A non-violent and eco-friendly method of sodium processing with potential applications in the course of sodium cooled fast breeder reactor operations as well as during their decommissioning has just been developed. While 2 M Epsom solution is recommended for peaceful sodium dissolution, dilute (<1 M) and super-saturated (>2.7 M) solutions can cause violent reactions and hence must be avoided. The solid waste produced in the Epsom and NaOH processes are comparable provided the $Mg(OH)_2$ produced on sodium dissolution in Epsom is converted back to $MgSO_4$ with H_2SO_4. The waste produced being only mildly alkaline do not cause skin burns and can be disposed off/stored without any further processing unlike the case in caustic process. A 1.3 M Epsom solution sprayed with a high-pressure jet cleaner in a open yard easily removed the sodium (~ 1 kg) blocked inside a mild steel metal pipe. The above solution jet also dissolved peacefully residual sodium (~ 50 kg) collected on a metal tray after a sodium fire experiment within a few minutes. The real advantage of the Epsom process, namely the pH control would be fully realized in the sodium cleanup of reusable reactor components. This is much simpler, safer and environmental friendly technique than the presently used sodium clean up techniques such as alcohol/steam or dispersed water in inert gas or the electrometallurgical technique recommended in the case of sodium-bonded spent nuclear fuel.

Acknowledgments

The authors are thankful to Sri S.E. Kannan, Head, Engineering Safety Division, IGCAR for support rendered during sodium disposal work.

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