

Does Phosphate Restrain Reactivity of Salt Cake from Secondary Aluminum Production?

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Abstract. Salt cake is the byproduct of secondary aluminum production (SAP) and is often disposed in the United States using landfills. Due to high reactivity of salt cake to water, a considerable amount of flammable gases (e.g., hydrogen, and methane) might be release after landfill as well as temperature increase and heat generation. Reduce or restrain the reactivity of salt cake is important for the safety management of these wastes. Here provide solid evidences that inorganic phosphate treatment can significantly slow down the reactivity after salt cake react with water, including the temperature rise and gas generation, especially for hydrogen, in the laboratory scale. The efficiency is demonstrated to be related to the rate of phosphorus, phosphorus species, and the mineral phase of salt cake. The large scale researches are needed for the application.

Keywords: Aluminum Recycle; Gas, Hydrogen, Phosphate; Reactivity; Salt cake; Temperature.

1. Introduction

The end-of-life management of solid wastes from secondary aluminum processing (SAP) is becoming not only a problem in the United States [1, 2], but a global problem [3-6]. In the North America, SAP is often completed in a rotary salt furnace with the addition of salt fluxes to improve recovery and reduce oxidation of the aluminum metal [2, 6]. The nonmetallic solid byproduct residue that results from such furnace waste is frequently termed “salt cake”, and contains 3 to 10% residual metallic aluminum [2, 7, 8]. Nearly 5 million tons of furnace waste (including salt cake) have been generated worldwide each year [9], almost one million tons of salt cake is disposed of in landfill annually in the United States [10].

Some landfills in the U.S. after disposal salt cake from SAP have reported operational issues. Temperatures in landfill gas wellheads were reported to be 60 to 93°C over a period of several months to several years[11], high concentration of hydrogen (H₂) (30 -50%) with gaseous ammonia (NH₃) (up to 15000 ppmv) were observed in a landfill [11]. Recently investigation on the characteristics and reactivity of salt cake from SAP further confirmed that salt cake from SAP contain considerable amount of metallic aluminium, nitrides, carbides and various oxides [2]. These metallic Al can liberate hydrogen (H₂); carbide produce methane (CH₄); and nitride form ammonia (NH₃) after salt cake exposed to liquids with the exothermic reactions [2, 12]. As results of these reactions, landfill fire and the high rates of landfill settlement/subsidence, as well as contaminations of heavy metals in soil and ground waters were also frequently occurred [13-15]. Therefore, it is very important to prevent or inhibit the reactivity of these wastes in the landfill environment. Here we report preliminary approach to employ inorganic phosphate in laboratory scale. High reactivity salt cakes were selected from different facilities throughout America.

Experimental Procedures

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1.1. Reactivity Evaluation

The reactivity was determined by the temperature increase and gas generation after salt cake reaction with different liquids. It was found that the released heat from the salt cake reacted with DI water was positively correlated with the productivity of hydrogen and the maximum temperature rise (ΔT_{\max}) [2, 12].

A 10-g salt cake sample was placed into a 60 mL volatile organic analyte (VOA) vial. After purging the vial with argon for 5 min, the vial was sealed and 10 ml pre-heated liquid was then added to the vial to achieve 1:1 liquid to solid ratio. The experiments were conducted at elevated environmental temperature conditions (37 °C or 50 °C) with an incubator (Fischer Scientific Isotemp Dual CO₂ Incubator). Usually, 6 to 12 sample vials and 1 control sample vial were grouped as one set arranged in an insulated box inside the incubator [12].

The gas composition and gas productivity were assessment after salt cake reacted with liquids with the fixed liquid to solid ratio (20:1) at elevated environmental temperature conditions (37 °C or 50 °C) with an incubator for 5 days. The gas volume was measured using 60 mL gas-tight syringe. The concentrations of hydrogen (H₂) and methane (CH₄) gas content were determined using an Agilent 6980 Gas Chromatograph equipped with a thermal conductivity detector (GC/TCD). It was found that the dominate component of generated gas was hydrogen and methane. The sum of H₂, and CH₄, was assumed as the net gas productivity of each treatment (ml g⁻¹ salt cake) in this study [12].

1.2. Salt cake Sampling, Mineral Phases and Reactivity

Different reactivity salt cake samples were selected for this study based on the mineral phases and reactivity of 39 salt cakes, which were collected from 10 secondary aluminum-processing facilities throughout America to cover a wide range of processes. It is a part of systematic study on the characteristics of salt cake and evaluation of salt cake waste reactivity in America when exposed to water, collaboration with the Aluminum Association and the Environmental Research and Education Foundation [12].

TABLE I. DOMINANT MINERAL PHASE (%) AND REACTIVITY IN SELECTED SALT CAKE SAMPLES

Sample ID	Al	Total	AlN	Total	ΔT_{\max}^*	$t_{\max T}^*$	Heat*	H ₂ * (m ³	CH ₄ *
		AIN		Al ₂ O ₃	(°C)	(h)	(GJ ton ⁻¹)	ton ⁻¹)	(m ³ ton ⁻¹)
2502-F	5	7.8	5	38	51	1.1	1.7	48	93
2046-H	2	13	10	40	24	2.2	2.3	11	3.6
2555-H	2	12	10	36	17	2.7	1.0	9	2.6
2512-J	4	6.9	3	47	9	0.9	1.5	32	2.5
2490-L	3	7.8	5	36	22	1.5	0.8	11	1.6
2601-M	6	4.8	2	32	64	0.5	2.7	71	6.8
2613-M	14	5.4	3	26	40	1	4.0	168	0.9

*Experiment setting: 10 g/10 ml DIW, 37°C, <2 mm for temperature profile; 5 g/5 ml DIW, 37°C, <0.05 mm for heat; 5 g/100 ml DI Water (pH6.2), 50°C, <2 mm, 5 days for gas productivity.

The dominant mineral phases and reactivity of selected SC were tabulated as Table 1. The medium abundance of Aluminum and total aluminum nitride in the studied 39 salt cake samples was 2 and 8%, respectively [2, 12]. The medium net gas productivity, heat, and ΔT_{\max} at 37°C environmental conditions of 39 salt cake samples was 24 m³ ton⁻¹, 0.8 GJ ton⁻¹, and 15°C respectively [12]. These indexes suggested that the selected samples were highly reactivity.

2. Results

2.1. Temperature Profile

Most salt cake samples have a single peak of temperature after reacted with deionized water (DIW, pH 6.2). The increased was related to the mineral phases of salt cake and liquid composition [12]. In general, the increased temperature was enhanced with the high pH conditions, but seemed to be repressed under the acidic environments, and with the dissolved organic matters in liquids (Table 2). Temperature profiles were further changed when the liquids contained inorganic phosphate, the ΔT_{\max} was decreased and the time to get

the maximum temperature ($t_{\max T}$) was also significantly delayed, and even several small peaks occurred after Na_2HPO_4 and NaH_2PO_4 injected (Figure 1).

TABLE II. IMPACT OF LIQUID COMPOSITION ON TEMPERATURE PROFILES OF SALT CAKE*

Liquids	ΔT_{\max} ($^{\circ}\text{C}$)			$t_{\max-T}$ (h)		
	2502-F	2555-H	2613-M	2502-F	2555-H	2613-M
0.1 M HCl	32	14	28	2.0	3.6	1.5
0.1 M NaOH	56	20	54	0.9	2.3	0.6
DIW	50	19	43	1.1	2.7	1.0
0.1M H_3PO_4	12	6	8	3.7	4.9	5.1
Landfill leachate	12	9	13	3.0	3.7	2.2
2% Humic acid salt	3	7	15	12	4.5	1.9
0.2 M NaH_2PO_4	7	4	10	4.1	6.0	17
0.2 M Na_2HPO_4	11	9	28	2.2	2.5	7.5

*Experiment setting: Liquid to solid ratio 1:1, 10 ml/10 g, 37 $^{\circ}\text{C}$, <2 mm, 5 day.

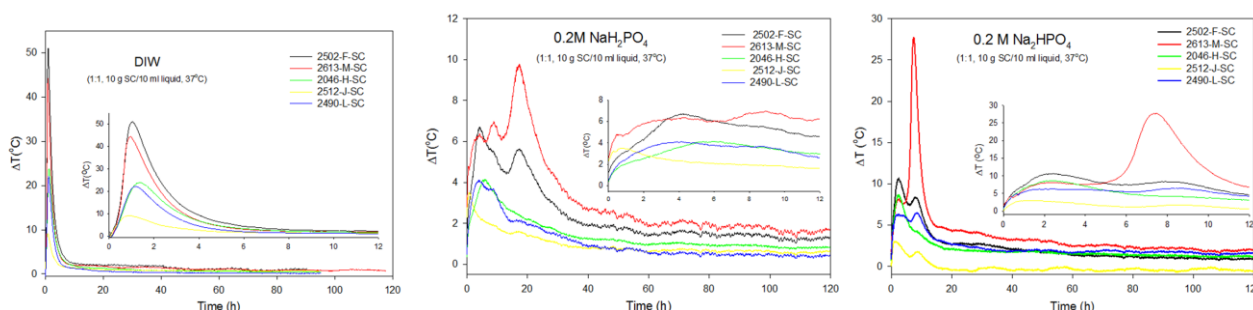


Fig. 1: Effect of phosphorus species in liquids on the temperature profiles of selected sack cake samples

(Experiment setting: Liquid to solid ratio 1:1, 10 ml/10 g, 37 $^{\circ}\text{C}$, <2 mm).

The changes were related to the phosphate species and concentration of phosphate. In fact, the rises of temperature were also significantly decreased even salt cake mixed with the solid phosphate salt (Figure 2a), or the materials contained phosphate (e.g. phosphate gypsum, Figure 2b). The higher phosphate, the low temperature increases were observed. It is noted that phosphate treatment also can efficiency control temperature change, even at the large particle size sample (<9 mm, Figure 2b), it is known that particle size is also one factor to change temperature profiles due to the reaction surfaces[12]. It should point out that temperature rise still occur in the all phosphate treatments, however, the rise were decreased as well as the time to get the peak were extended. Therefore, the intensity of reactivity of salt cake in phosphate treatments were reduced based on the response of temperature changes.

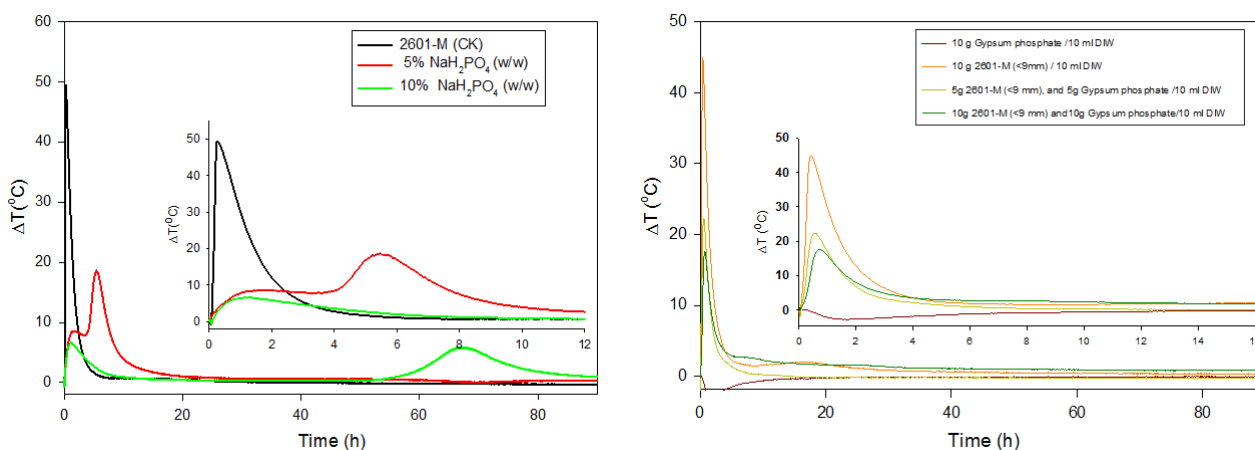


Fig. 2: Effect of mix solid phosphate with salt cake on the temperature profile at 50 $^{\circ}\text{C}$

(Experiment setting: Liquid to solid ratio 1:1, 10 ml DIW/ 10 g solids, 50 $^{\circ}\text{C}$, a: <2 mm, b: <9 mm).

2.2. Gas Generation

Gas were generated after salt cake reacted with liquids, and the dominate gas was hydrogen, not methane[2, 12]. Hydrogen is an explosive gas with an explosive range (in air) of 4-79% and as a result can potentially cause fires. Hydrogen is even of greater concern if generated in municipal solid waste (MSW) landfills. Apart from being a fire hazard when mixed with CH₄, landfill gas collection systems are not designed to handle H₂ since MSW landfill gas generally consists of CH₄ and CO₂ at 50/50 ratio [12]. As expected, gas productivity was related to the liquid composition (Table 3). It is interesting to note that most differences were hydrogen, not methane. In other words, the most dangerously gas from reactivity of salt cake can be adjustable based on the reacted composition of liquids. Similar to the temperature change, hydrogen productivity was significantly reduced in the phosphate treatments, through it is related to phosphate concentration, phosphate species, and mineral phases in the salt cake (Figure 3). For example, sample 2613-M, one of the highest hydrogen generator, still can release considerable amount of hydrogen.

TABLE III. IMPACT OF LIQUID COMPOSITION ON THE GAS PRODUCTIVITY OF SALT CAKE *

Liquids	Hydrogen productivity (ml/g)			CH4 productivity (ml/g)		
	2555-H	2489-L	2613-M	2555-H	2489-L	2613-M
0.1 M HCl	16.3	4.4	57.8	3.5	2.0	0.6
0.1 M NaOH	16.8	66.2	148	3.5	3.0	1.4
DIW	14.0	49.2	59.3	3.7	1.9	0.9
Landfill leachate	1.2	0.0	48.6	1.5	1.1	0.7
2% Humic acid salt	10.4	0.8	60.1	3.5	2.0	0.4
0.2 M NaH ₂ PO ₄	1.4	0.2	22.9	1.3	0.6	1.1
0.2 M Na ₂ HPO ₄	0.5	0.7	42.1	3.5	1.2	1.8

*Experiment setting: Liquid to solid ratio 20:1, 20 ml/1.0 g SC, 50°C, <0.05 mm, 5 day.

The role of phosphate on the hydrogen productivity of salt cake is unknown. Our previously work have demonstrated that the hydrogen generation from the reaction of metallic aluminium with water was related to the trigger effect of AlN and/or Al₄C₃[12]. Both of AlN and Al₄C₃ can be easily reacted with water to release ammonia and methane, and their byproducts of aluminium hydroxides can significantly promote the hydrolysis of water by reaction of metallic aluminium. It is documents that phosphate can significantly inhibit the hydrolysis of aluminum nitride, as results, the mineral phasers of aluminum hydroxide were changed [16-18]. This might be the reasons why the hydrogen productivity of salt cake in phosphate treatment was significantly reduced, as consequences, the temperature rise from salt cake reaction also decreased.

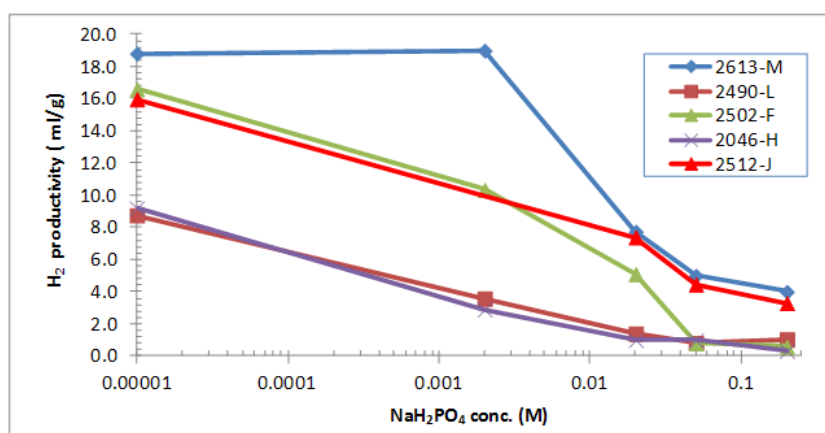


Fig. 3: Effect of phosphate concentration in liquids on the hydrogen productivity of salt cake at 50°C (Experiment setting: Liquid to solid ratio 20:1, 20 ml DIW/ 1 g SC, 50oC, <9 mm, 5-day, NaH2PO4).

3. Conclusions

Salt cake from SAP is usually dumped with MSW landfill in American. Hydrogen generation, temperature change and heat release after disposal in landfill can cause a lot of troubles. Here provide the solid evidences by laboratory experiments that phosphate treatment can significantly reduce the production of hydrogen and as consequence, the temperature change was restrained after salt cake react with water. The efficiency is related to the phosphorus species and the rate of phosphorus, as well as the mineral phase in salt cake. It is highlight for the new strategies for safe management of the municipal landfill for salt cake from secondary aluminum production. Additional work is necessary to understand the mechanism of phosphate effect and the other availability for other low-cost phosphorus recourses. Large scale experiments are also needed for the application.

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