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Study of degradation and heat of dissolution of solids in aqueous blend of AMP and KSAR loaded with CO_2

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Abstract

An example of a novel precipitating solvent system (NPSS) developed at SINTEF [1] has been further characterized in this work. Chemical stability under thermal and oxidative conditions have been measured to respectively 12 % and 8 % loss of amine and aminoacid. The results were compared with literature data for single solvent components (AMP, sarcosine) or blends containing one of the components. Further, in order to estimate heat requirements for the dissolution of precipitate formed in the absorber, heat of dissolution of solids in water and in unloaded AMP-KSAR solution has been measured at 40 ºC in a reaction calorimeter CPA202. The results show that about 2 times less heat is required to dissolve the precipitate formed with NPSS, AMP bicarbonate, compared to potassium bicarbonate crystals when dissolution is in water. At the same time, heat of dissolution of the NPSS precipitate into the unloaded AMP-KSAR solution is about 2 times lower than heat of its dissolution in water.

Keywords: Absorption; Carbon dioxide; Precipitating solvent system; Degradation; Heat of dissolution

1. Introduction

Phase-change solvent system has been identified as one of the emerging post combustion technologies with potential to reduce cost [2]. Several studies have proposed different precipitating phase-change solvent system for

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CO_2 capture [3]. Data on solvent stability and heat requirement for dissolution of the precipitated solid are necessary for characterization of such systems.

Solvent degradation is one of the drawbacks on promising post combustion CO_2 absorbents including amines and amine/amino acids systems since this results in solvent loss, operational issues with regard to heat stable salts or corrosion and emission. Normally the degradation in reactive absorption systems is divided into thermal degradation with or without CO_2 present or oxidative degradation. Thermal degradation of a large set of amines has been studied by several research groups over a long period of time [4]-[6] while oxidative degradation has received increased attention in the last decade [7]-[10] as it was discovered that oxidative degradation compounds are the main products under real plant conditions [11][12]. In this work chemical stability under thermal and oxidative conditions for a blend amine, of 2-amino-2-methyl-1-propanol (AMP) and amino acid salt, potassium sarcosine (KSAR) is given and compared against literature data on degradation of single component AMP, SAR or blends containing one of the components [5][9][13]-[15].

This work carried out further characterization of NPSS [3], a blend of amine and amino acid salt to determine the extent of its stability in terms of oxidative and thermal degradation. Further, the heat requirement for dissolution of the precipitant solid was measured.

Nomenclature

t	temperature, ºC
ΔH_{diss}	heat of dissolution, J/mol
m	mass, g
α	CO_2 loading, mol-CO_2/mol-amine

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2. Experimental

2.1. Chemicals

Chemicals used in this work (Table 1) were used as received without further purification. Aqueous solutions were prepared gravimetrically using distilled de-ionized water. The NPSS, a blend of AMP and KSAR, was prepared as described in [20].

Table 1. Chemicals used in this work

Chemical name	CAS number	Purity	Supplier
2-Amino-2-methyl-1-propanol, AMP	124-68-5	99 %	Acros Organics
Sarcosine, SAR	107-97-1	≥ 98.0 %	Fluka
Taurine	107-35-7	≥ 99.0 %	Fluka
Potassium hydroxide, KOH	1310-58-3	≥ 85 %*	Carl Roth GmbH
Potassium carbonate, K2CO3	584-08-7	≥ 99.0 %	Sigma-Aldrich

* Concentration checked by titration with 1N H_2SO_4

2.2. Experimental set-ups and procedures

2.2.1. Solvent degradation study

Two different set-ups are used for the degradation experiments; oxidative degradation using an open-batch reactor (Fig 1. a) and thermal degradation using cylinders (Fig. 1, b). Both set-ups are explained in detail in [12]. The oxidative degradation set-up consist of a jacketed humidifier, jacketed glass reactor (1kg liquid volume, Fig 1. a), two condensers, mass flow controllers and gas pump. A gas flow of air (0.35 L/min) and CO_2 (7.5 mL/min) is continuously added to a recycle loop with a recirculation rate of 50L/min. The gas is bubbled through the solution, which is kept at 55 °C for 3 weeks. The gas leaving the system is bubbled through a solution of H_2SO_4 (0.25M). Samples are collected regularly and analyzed. The thermal degradation set-up consists of stainless steel cylinder with a liquid volume of 15 mL, Fig 1. b. These cylinders were kept at constant temperature of 135 °C for 5 weeks using a convection oven. Samples are collected by removing one cylinder from the oven each week. In both experiment a pre-loaded solution ($\alpha = 0.2$ mole CO_2 per mole of amine+aminoacid salt) was introduced.
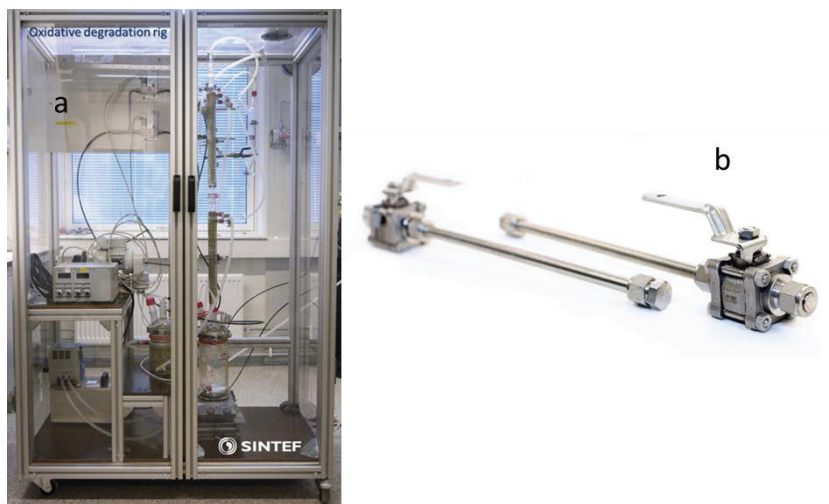

Fig. 1. (a) Open batch oxidative degradation rig; (b) stainless steel cylinders used for thermal degradation

Analyses for alkalinity (titration with 1N H_2SO_4), CO_2 (Total organic carbon using Apollo), AMP and SAR were conducted for all samples in both experiments. For AMP and SAR the analyses were conducted on a LC-MS /MS 6460 Triple Quadrupole Mass Spectrometer coupled with a 1290 Infinity LC Chromatograph and Infinity Autosampler 1200 Series G4226A from the supplier Agilent Technologies [16]. Samples from the cylinders were in addition analyzed for metals (Fe, Cr and Ni, all samples) using ICP-MS while samples from the open batch reactors were analyzed for water (Karl Fischer titration, all samples), density (Mettler Toledo CM40 at 22 °C, start sample) and organic nitrogen (Kjeldahl method, end sample).

2.2.2. Heat of dissolution measurements

Information on heat necessary for dissolving the solids is required in precipitating process design and can contribute to capture energy demand. Further, such data is required for proper modelling and simulation of the solvent based capture processes.

Heat of dissolution of precipitated solid in AMP/KSAR system was measured in this work using a commercially available calibration-free reaction calorimeter CPA 202 [17]. The setup (Fig. 2) is operated at temperatures between 25 and 130°C and at pressures from vacuum to 10 bar. The reactor is submersed in the CPA202BU thermostat filled with diethylene glycol as a heating media. A 250 ml glass reactor is equipped with a Pt-100 temperature sensor (accuracy 0.1 ºC), a magnetic stirrer and a batch injector allowing injecting the solids and mixing them with the liquid in the reactor at isothermal conditions. All operation parameters (e.g. reactor temperature, heat flow, etc.) are recorded as function of time using a ChemiCall software provided by Chemisens. Sensitivity of the calorimeter given by the producer is 0.1 W.
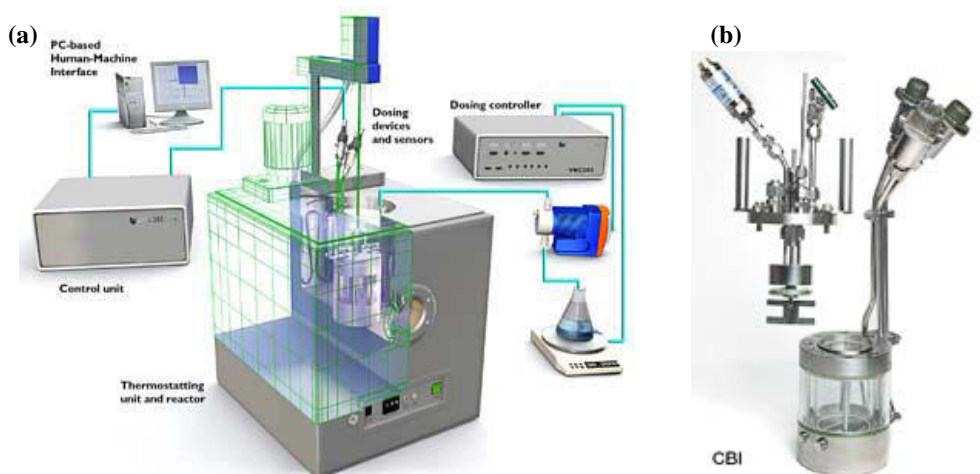
Fig. 2. (a) The CPA202 Reaction Calorimeter setup; (b) reactor and a batch solids injector (www.chemisens.com)

Solids crystals were prepared by bubbling CO_2 through the AMP/KSAR solution until desired CO_2 loading is reached. A sample of liquid and solid formed is collected as a slurry, the slurry is filtered (to remove the liquid) and the solid dried by vacuum filtration for heat of dissolution study. Solids at 4 different CO_2 loadings were prepared: α = (0.3, 0.35, 0.40, and 0.44) mol-CO_2/mol-amine. Amine concentration (total alkalinity) in the prepared solution was checked by titration with 1N H_2SO_4, while concentration of CO_2 was analysed as TOC (total organic carbon) using APOLLO.

For measuring heat of dissolution, the reactor was filled with 120-125 g solvent (water or unloaded AMP/KSAR solution). 1.5-2g solid was placed in the batch injector of solids. The reactor with the injector was installed in the thermostat bath and heated to the set temperature. It was assumed that the system reached equilibrium when no change in temperature (±0.01 ºC) and heat flow (±0.03 W) was observed for at least 10 min. At equilibrium, the solids were injected into the liquid and the system left to reach a new equilibrium. The amount of solid and liquid in the reactor was selected so that change in the alkalinity (ionic strength) of the solvent after addition of solid was below 0.1 mol/kg-solvent. When water used as a solvent, this concentration is often defined as infinite dilution (activity coefficient may be assumed equal to 1).

An example of the on-line heat flow data for taurine injection into water is presented in Fig. 3. Heat of dissolution was calculated from the amount of heat added or removed by the instrument to keep the systems at isothermal conditions:

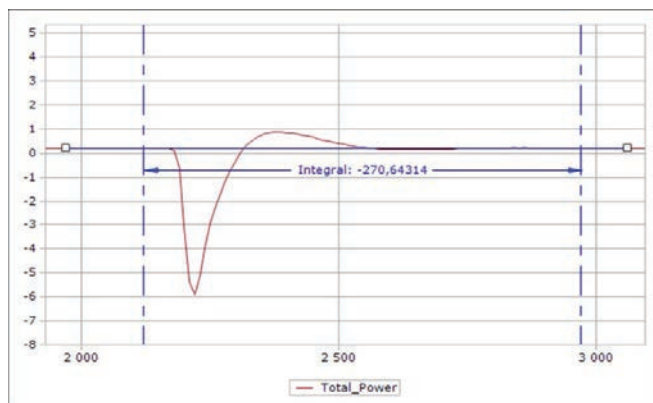$$\Delta H_{diss} = \frac{\int Heat\_flow}{m_{solid}}$$

(1)

Fig. 3. An example of on-line heat flow data from the reaction calorimeter for taurine injection into water

3. Results and discussion

3.1. Solvent degradation

The duration of the oxidative degradation experiment was 3 weeks and the data for the experiment is given in Table 2.

Table 2. The data from the oxidative degradation experiment. (α is calculated using data from titration results.)

Time (days)	LC-MS		Titration		Karl Fisher	Density	Kjeldahl
	Sarcosine (Loss, %)	AMP (Loss, %)	Amine (Loss, %)	CO_2 (α)	Water (wt%)	g/mL	wt% N
0.0	0	0	0	0.19	37.41	1.148	NA
0.9	3.6	5.7	2.7	NA	37.84	NA	NA
3.8	7.9	4.2	5.4	NA	37.33	NA	NA
6.9	7.5	5.5	6.2	NA	37.48	NA	NA
10.9	8.9	7.2	8.5	NA	39.26	NA	NA
14.1	9.8	7.4	8.3	NA	39.45	NA	NA
17.8	10.4	7.4	8.3	NA	39.49	NA	NA
20.8	9.8	7.6	8.8	0.35	39.65	NA**	7.17*

NA = not analyzed
*Sample diluted, then analyzed, given number takes into account the dilution
**Not analyzed due to precipitation

The water analysis shows that the water level increases over time. This is likely related to the wet gas entering the system. It is known from previous work that the level of water in the wetting chamber influences the mass balance in the system giving increase or decrease of water in the system. In this case, a gain of mass (water) was observed. The loss of SAR and AMP (%) as a function of time (days) is given in Fig. 4.
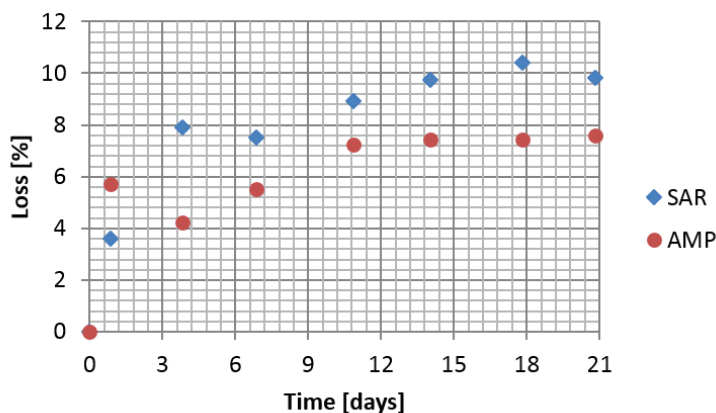
Fig. 4. Concentration of SAR and AMP (mol/L) as a function of time (days).

From raw data a loss of SAR on 10 %, 8% of AMP, and 8 % of total amine (amine + aminoacid from LC-MS) over 21-days period is observed. Both water and CO_2 ended at a higher concentration than the initial, this means that the loss of amine observed in this experiment is an effect of degradation and dilution. It is therefore expected that the amine loss caused by degradation is less than the given numbers. The loss of SAR (detected by LC-MS) is slightly higher than was observed for KSAR using a closed batch set-up as described by [9].

Amine concentration in initial sample determined by titration, corresponds well with analysis results for sarcosine and AMP determined by LC-MS. The CO_2 concentration increases over time which is explained by the continuous gas flow of CO_2 added throughout the experiment. In this experiment, the initial loading was 0.2 mol-CO_2/mol-amine (calculated using CO_2 and amine concentration from titration results).

The overall evaluation of the system shows an amine loss of less than 10% which is slightly lower than for MEA [16]. A nitrogen balance for the end sample showed the organic nitrogen is accounted for as AMP and SAR taking into the account sampling and analytical uncertainties.

An evaluation of emission of AMP and SAR is conducted by bubbling the gas fraction leaving the system through sulfuric acid (0.25M). The pH of the solution is measured regularly and the acid is switched twice during the three-weeks period: on day 7 and 14. A total of less than 5 mmol of AMP and less than 3E-05 mmol of SAR were collected for this experiment.

The thermal degradation experiment was conducted over a 5-weeks period. The data for the experiment is given in Table 3.

Table 3. The data for the thermal degradation experiment, loss specific components analyzed by LC-MS, loss of amine measured using titration, loading of CO_2 (α is calculated using data from titration results) and density (NA = not analyzed).

Time (weeks)	LC-MS		Titration		g/mL
	Sarcosine (Loss, %)	AMP (Loss, %)	Amine (Loss, %)	CO2 (α)	Density
0	0.0	0.0	0.0	0.20	1.148
1	31.5	0.2	2.1	0.19	NA
2	29.0	0.6	2.5	0.19	NA
3	29.9	1.4	2.0	0.18	NA
4	28.3	2.9	2.2	0.18	NA
5	28.9	2.5	2.3	0.18	1.133
5	29.4	2.9	2.3	0.18	1.153

The samples (not week 0) had a lot of precipitate. The ICP-MS results (samples tested with and without centrifugal treatment) indicate that the precipitate is iron. Iron is present in highest amounts. After 5 weeks the

concentration of chromium, iron and nickel was respectively 40, 2300 and 520 mg/L. The high metal concentration is likely a result of the high conductivity and ion strength of amino acid salt solutions [13]. For iron, the major change occur between the initial sample and week 1 sample, after week 1 the slope decreases dramatically. This could indicate that the solubility of iron in the solution reaches it maximum. The high metal concentration observed in this experiment correspond well with literature data for experiments with KSAR [5][13]. The loss of SAR and AMP (%) as a function of time (weeks) are given in Fig. 5.
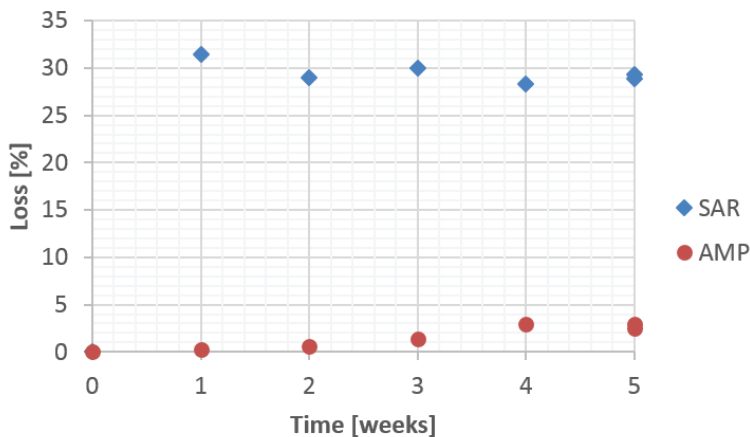

Fig. 5. The loss of SAR and AMP [%] (analytical data from LC-MS) as a function of time [weeks] in thermal degradation test.

The loss after 5 weeks based on analytical results from LC-MS (SAR and AMP) was 12 % and from total amine (titration) 2 %. This deviation is likely related to formation of degradation compounds that also have amine functionality and shows the importance of conducting analyses of each amine component as well as total amine (titration) especially for thermal degradation experiments where carbamate formation is expected. Data from literature [5][13] for the single amine systems (AMP or SAR using KSAR) is available. Direct comparison is however difficult since initial CO_2 concentration varies and for thermal degradation experiments amine loss increases with CO_2 concentration. The overview of loss for these experiments is given in Table 4.

Table 4. Amine loss for the different experiments.

Experiment	Comment	Component	Loss [%]
This work	Blend ($\alpha = 0.2$ mole CO_2 per mole of amine+aminoacid salt)	SAR	29
		AMP	3
Eide-Haugmo [5]	Single component system ($\alpha = 0.5$ mole CO_2 per mole of aminoacid salt)	SAR	46
Eide-Haugmo [5]	Single component system ($\alpha = 0.5$ mole CO_2 per mole of amine)	AMP	5
Vevelstad [13]	Single component system (($\alpha = 0.4$ mole CO_2 per mole of aminoacid salt)	SAR	33

The results for the blend shows that SAR is more susceptible toward thermal degradation with CO_2 than AMP. The actual CO_2 concentration (mol/kg) in the solution for this experiment and for the single experiment SAR described by Vevelstad [13] is comparable which explains the comparable amine losses. The higher CO_2 concentration (estimated to be 1.5 of CO_2 concentration in this work) in Eide-Haugmo's [5] experiments could explain the higher amine loss compared to this data and the experiment by Vevelstad [13].

3.2. Heat of dissolution

No data were found in literature for the heat of dissolution of sarcosine or potassium bicarbonate. Therefore, heat of dissolution of taurine and potassium carbonate was measured in this work and data compared to the values found in literature (Table 5). It may be seen from the table that heat of dissolution of taurine is slightly lower than values reported, while results for the potassium carbonate is similar to the values reported by Bichowsky and Rossini (1936). It may be seen from the table that dissolution of taurine is an endothermal reaction (positive value for the ΔH_{abs}), while heat is released at dissolution of the potassium carbonate in water (negative value for the ΔH_{abs}). In this work, heat of dissolution of the prepared solids (precipitates at different CO_2 loadings) are compared with the heats of dissolution of pure sarcosine and potassium bicarbonate measured at the same conditions.

Table 5. Heat of dissolution of taurine and potassium carbonate in water

Solid	ΔH_{diss} in water, kJ/mol		
	25 ºC	40 ºC	Ref (25 ºC)
Taurine	23.39	22.24	25.02 [18]
	23.39	22.14	
Potassium carbonate, K2CO3	-27.78	-31.13	-27.61 [19]
	-27.83	-30.49	

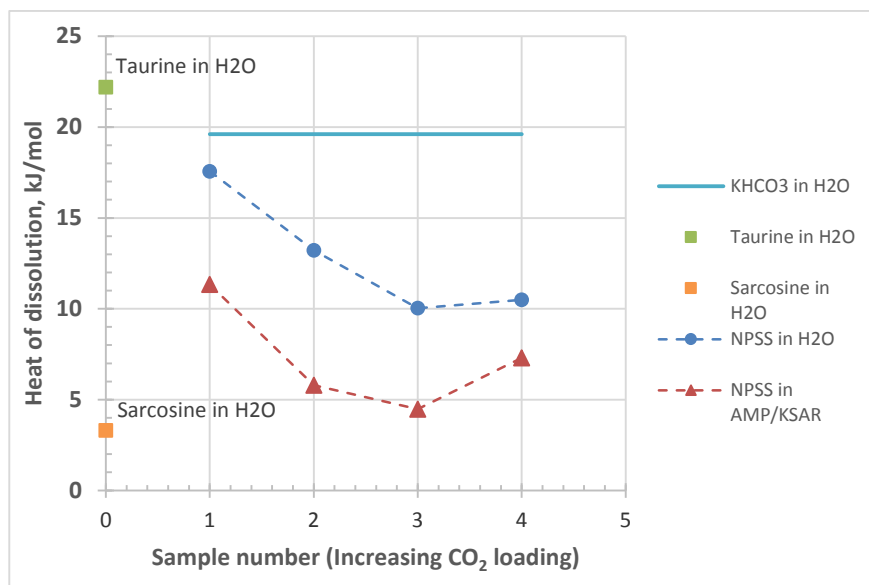The results from this work presented in Fig 6 and Table 6.

Fig. 6. Heat of dissolution of solids in water and in AMP/KSAR solution measured in this work at 40 ºC

Table 6. Heat of dissolution of solids in water and AMP/KSAR solution at 40 ºC

Solid	m*, mol/kg-solvent	ΔHdiss in water kJ/mol	ΔHdiss in AMP/KSAR kJ/mol
Sarcosine	0.103	3.31	-
KHCO$_3$	0.100	19.61	-
Precipitate, $\alpha = 0.30$		17.57	11.33
Precipitate, $\alpha = 0.35$		13.22	5.79
Precipitate, $\alpha = 0.40$		10.03	4.48
Precipitate, $\alpha = 0.44$		10.50	7.29

* concentration of the liquid phase after adding solids

Taking into account that KHCO$_3$ is the only product formed when K$_2$CO$_3$ reacts with CO$_2$, it may be seen from the data that heat of dissolution of potassium bicarbonate in water is higher than heat of dissolution of pure sarcosine or NPSS precipitate (about two times higher) tested in this work. Further, the crystal heat of dissolution is seen to be about two times lower when the solid is dissolved in the AMP/KSAR solvent than when dissolved in water. Heat of dissolution decreases slightly for the precipitates collected at loadings 0.3 to 0.4, but increases at loading 0.44 that may be explained by formation of potassium bicarbonate in the NPSS solution at this loading [20].

4. Conclusions

Oxidative and thermal degradation tests for the NPSS solvent show that the overall amine loss at both thermal and oxidative degradation conditions is slightly lower than that for 30 wt% MEA. AMP is more stable than SAR under both conditions; however at oxidative conditions the difference is small. A high iron concentration was observed, which is likely connected to the high conductivity and ion strength of the solution.

Heat of dissolution of precipitate formed in the studied solution upon CO$_2$ loading is much lower than that of potassium bicarbonate indicating that less heat is required for the solids dissolution in the process.

Acknowledgements

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