Full Length Article

Study on a new wet flue gas desulfurization method based on the Bunsen reaction of sulfur-iodine thermochemical cycle

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HIGHLIGHTS

- A new wet FGD method based on the Bunsen reaction was developed.
- I_2/HI absorption system exhibited great SO_2 removal performance.
- The absorption products are H_2SO_4 and HI.
- H_2SO_4 has better market prospect than traditional wet FGD products.
- HI could be used as the raw material for hydrogen production.

GRAPHICAL ABSTRACT
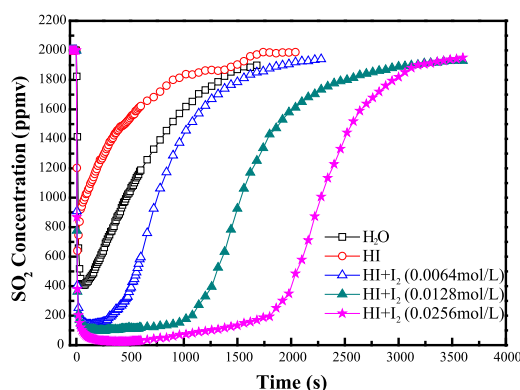
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ABSTRACT

A novel wet flue gas desulfurization method based on the Bunsen reaction of sulfur-iodine (SI) thermochemical cycle was investigated in this paper. I_2 and HI absorption system was utilized to remove SO_2 from simulated coal-fired flue gas. The SO_2 removal efficiency was about 98.8% when the I_2 concentration was 25.6 mmol/L. The influences of reaction temperature, initial SO_2 concentration and the other flue gas components on SO_2 removal were investigated, respectively. The absorption products were H_2SO_4 and HI, which could be easily separated by distillation. Compared with the traditional wet flue gas desulfurization (FGD) byproducts, such as gypsum or magnesium sulfate, H_2SO_4 has better commercial value and application prospect. Moreover, HI could be used as the raw material for the hydrogen production in the SI thermochemical cycle. In short, it is a promising technology for the SO_2 removal and recycling from coal-fired flue gas.

1. Introduction

Sulfur dioxide (SO_2) is one of the major air pollutants released from the coal combustion. In the past decades, a great deal of SO_2 is emitted to the atmosphere because of the increasing coal consumption [1]. The emission of SO_2 resulted in serious environmental problems, such as acid rain and fine particles [2]. Therefore, the flue gas desulfurization (FGD) is essential for environmental protection.

The common FGD methods include dry FGD, semidry FGD and wet FGD [3]. Among them, wet FGD technology has been employed widely due to its simplicity and high efficiency [4]. Generally, a slurry of alkaline sorbents, such as limestone, magnesium hydroxide or ammonia, are utilized to absorb and remove SO_2 from flue gas [5–7]. Nevertheless, the byproducts yielded in the wet FGD

process, such as gypsum, magnesium sulfate or ammonia sulfate, have become a big burden because of their poor market [8]. Thus, it is significant to develop a new FGD technology whose byproduct has higher economic value or better market prospect than the traditional wet FGD byproducts. In another FGD system, SO_2 could be converted into sulfuric acid [9]. Sulfuric acid is the largest-volume industrial chemical produced in the world. Furthermore, the consumption of sulfuric acid is often used to assess the industrialization degree of a country [9,10]. It will bring higher economic benefits than the common wet FGD technology if the SO_2 in coal-fired flue gas could be converted to H_2SO_4. But the double contact process, the major manufacturing method in sulfuric acid production industry, is always employed when the SO_2 concentration is high (above 4.4%) [11–13]. This precondition limited the application of the double contact process in SO_2 removal and recycle from coal-fired flue gas because the SO_2 concentration of coal-fired flue gas is relatively low (about several thousand ppmv) [14–16]. Hence, it is meaningful to find a new method for removing low concentration SO_2 from coal-fired flue gas and converting it to H_2SO_4.

In recent years, sulfur-iodine (SI) thermochemical cycle attracted lots of attention in hydrogen production. It is believed as a promising and efficient technique for thermochemical hydrogen production [17]. The whole SI cycle technique consists of three parts:

$$I_2 + SO_2 + 2H_2O = 2HI + H_2SO_4 \tag{R1}$$

$$H_2SO_4 = H_2O + SO_2 + 1/2O_2 \tag{R2}$$

$$2HI = I_2 + H_2 \tag{R3}$$

R1 is known as the Bunsen reaction. SO_2 is absorbed by I_2 solution and produce H_2SO_4 and HI. Then the two acid solutions are separated into H_2SO_4 phase and HI phase. Finally, H_2SO_4 is decomposed into SO_2, H_2O and O_2. And the HI is decomposed into H_2 and I_2. In the whole SI process, water is decomposed into H_2 and O_2. Moreover, SO_2 and I_2 could be totally recycled [18]. However, there are still some challenges for SI cycle. For example, the H_2SO_4 should be decomposed under high temperature to recycle the SO_2 which require a large amount of energy [19]. Meanwhile, a stable and active catalyst is also needed for sulfuric acid decomposition [20]. These challenges limited the industrial application of SI thermochemical cycle. As a matter of fact, the decomposition of HI is the key step for hydrogen production. Recycling the SO_2 through the decomposition of H_2SO_4 is probably not necessary when there is enough SO_2 take part in the Bunsen reaction to generate HI. While, the coal-fired flue gas could provide enough SO_2 for the Bunsen reaction. It will simplify the whole SI thermochemical cycle if the SO_2 in coal-fired flue gas could be utilized to produce HI through the Bunsen reaction. On the other hand, the Bunsen reaction could be used to remove the SO_2 from flue gas and produce H_2SO_4. Thus, it will be benefit for SO_2 removal from flue gas and hydrogen production. So far, the Bunsen reaction is mainly studied for the hydrogen production. There is few research that reported the SO_2 removal from the coal-fired flue gas based on the Bunsen reaction. Furthermore, the optimal experimental conditions of the Bunsen reaction are different to the actual conditions for the traditional wet FGD technology. It may not be suitable for the SO_2 removal from the coal-fired flue gas. In this paper, the feasibility of SO_2 removal method based on the Bunsen reaction was investigated. The influences of reaction temperature, initial SO_2 concentration, the other flue gas components and the accumulation of reaction products on SO_2 removal were investigated, respectively. Distillation was used to separate the main products of FGD (H_2SO_4 and HI). It is a promising technology to remove

and reclaim SO_2 from coal-fired flue gas. Furthermore, the HI generated through the Bunsen reaction could be used as the raw material of hydrogen production.

2. Materials and methods

2.1. Experimental setup and chemicals

The schematic diagram of the experimental apparatus is shown in Fig. 1. A three-neck flask (500.0 mL) was used as the adsorption reactor. A gas mixture containing N_2, O_2, SO_2 and NO was used to simulate the coal-fired flue gas. The concentrations of SO_2, NO and O_2 were 2000 ppmv, 1000 ppmv and 10%, respectively. These pure gases were supplied by the gas cylinders and the concentration of each flue gas component was controlled by mass flowmeters. In order to investigate the influence of actual flue gas components on SO_2 removal, the concentrations of NO and O_2 were adjusted, respectively. The simulated flue gas (2.0 L/min) passed through the three-necked flask which contained absorption solution (250.0 mL). The I_2/HI absorption solution was prepared by dissolving a certain amount of iodine in HI solution. The HI concentration is 75.0 mmol/L. And the I_2 concentration was from 6.4 to 25.6 mmol/L. The residence time for the simulated flue gas to pass through the absorption solution was approximately 7.5 s. The temperature of absorption solution could be adjusted from 298 to 353 K by the water bath. In addition, a hundred cycles of SO_2 absorption tests were performed to investigate the accumulation of H_2SO_4 and HI on SO_2 removal. After each run of absorption experiment, a certain of I_2 was added into the absorption solution to maintain the I_2 concentrations were 6.4 mmol/L, 12.8 mmol/L and 25.6 mmol/L, respectively.

The absorption solution after reaction was sampled and distilled at 408 K for 2 h to separate the main reaction products (HI and H_2SO_4). The original absorption solution, the distilled solution and residual solution were analyzed by ion chromatography to calculate the separation efficiency of HI and H_2SO_4.

The main chemicals employed in this research were HI (57.0%), I_2 (99.0%), H_2SO_4 (98.0%), NaOH (99.0%) and Ca (OH)$_2$ (99.0%) from Sigma-Aldrich Co. N_2 (99.9%), SO_2 (10.0%), NO (10.0%), and O_2 (99.9%) were from Dalian Date Standard Gas Co.

2.2. Analytical methods

The concentrations of SO_2, NO and O_2 in simulated flue gas were determined by flue gas analyzer (Kane KM900, UK) from the inlet and outlet of absorption reactor. The SO_2 removal efficiency (η) was defined as:

$$\eta = (C_{in} - C_{out})/C_{in} \times 100\% \tag{1}$$

where C_{in} and C_{out} are the concentrations of SO_2 at the inlet and outlet of adsorption reactor, respectively. Additionally, the reaction products were detected by ion chromatography (Metrohm, Swiss) and UV spectrophotometer (Persee T6-1650E, China).

3. Results and discussion

3.1. SO_2 adsorption by different solution

Generally, the water solubility of iodine is relatively low (about 29.0 mg at 293 K) [21]. But iodine is better soluble in iodide solutions. So, a certain amount of HI was added into the absorption solution to increase the solubility of iodine. The influence of I_2 concentration on the SO_2 removal was shown in Fig. 2.

From Fig. 2, it could be seen that it is difficult for the water or HI solution to remove SO_2 from flue gas. While, the iodine could
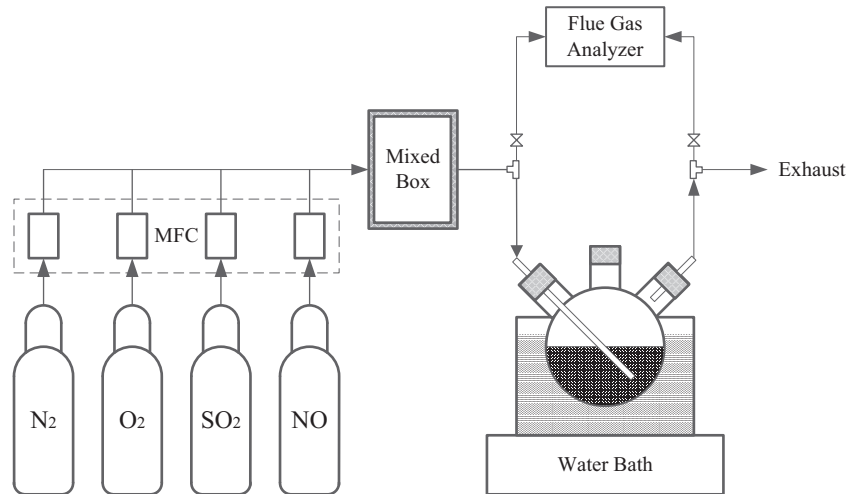
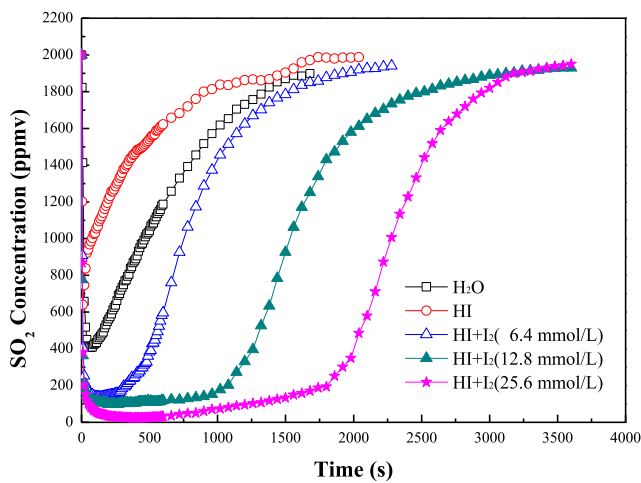Fig. 1. The schematic diagram of the SO_2 absorption experimental apparatus.

Fig. 2. The influence of I_2 concentration on the SO_2 removal.

enhance the SO_2 removal greatly. The removal efficiency of SO_2 increased from 93.1% to 98.8% when the I_2 concentration increased from 6.4 to 25.6 mmol/L. Obviously, more iodine could make the Bunsen reaction thermodynamically favorable [22]. In addition, I^- can react with iodine and form polyiodide species [23,24]. Accordingly, the gas-solid-liquid reaction between water, SO_2 and I_2 was transformed to a gas-liquid reaction among water, SO_2 and polyiodide species which accelerated the reaction rate [25]. Meanwhile, the amount of SO_2 removed from the simulated flue gas was nearly equal to the amount of I_2 in the absorption solution (Table A1), which inferred that almost all of the I_2 in the absorption solution reacted with the removed SO_2. According to the analysis results of reaction products (Fig. A1), the main reaction products are H_2SO_4 and HI which indicated the main reaction was Bunsen reaction. Furthermore, the SO_2 removal performance of I_2/HI absorption system was compared with the tradition wet FGD system (Fig. A2). The SO_2 removal efficiencies were very close when the absorbents were I_2/HI, NaOH and $Ca(OH)_2$, respectively. Hence, it is effective for I_2/HI absorption system to remove SO_2 and convert it into H_2SO_4.

3.2. The influence of absorption solution temperature

It is reported that the temperature of 330–350 K has been proposed as an optimal reaction temperature for the Bunsen reaction

[26]. However, the typical temperature of absorption solution in wet FGD system is usually below 323 K [27–29]. In order to investigate the effect of reaction temperature on the SO_2 removal efficiency, a series of experiments were conducted under different temperatures from 298 to 353 K. The SO_2 removal efficiency under different temperatures were shown in Fig. 3.

As can be seen in Fig. 3, the SO_2 removal efficiency increased from 93.1% to 98.0% when the temperature of absorption solution increased from 298 to 353 K. It seems that the higher temperature of absorption solution could enhance the SO_2 absorption. That may be explained by the endothermic property of the Bunsen reaction. Nevertheless, the total amount of removed SO_2 and utilization rate of I_2 were both higher when the temperature of absorption solution is lower (Table A2). Therefore, SO_2 could be removed efficiently by I_2/HI absorption system even at the typical absorption solution temperature of wet FGD system.

3.3. The influence of SO_2 concentration

In the researches of Bunsen reaction, the applied SO_2 concentration is always higher than 10% [30–32]. But the SO_2 concentration is much lower than 10% in coal-fired flue gas. It is necessary to investigate the SO_2 removal by I_2/HI absorption system when the SO_2 concentration is low. The SO_2 removal experiments were conducted under different SO_2 concentration.
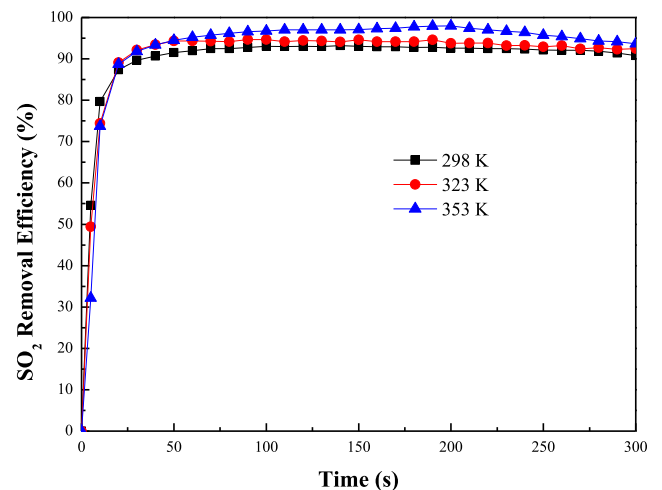

Fig. 3. The SO_2 removal efficiency under different temperatures.

From Fig. 4, it could be seen that the SO_2 removal efficiency was over 90% when its concentration was from 500 to 2000 ppmv. Meanwhile, the utilization of I_2 was also near 100% (Table A3). There is no remarkable difference on the SO_2 removal when its initial concentration is different. So, it is effective for I_2/HI absorption system to remove low concentration SO_2 from coal-fired flue gas.

3.4. The influence of flue gas components on SO_2 removal

The components of coal-fired flue gas are complicated. In order to identify the effect on the SO_2 removal by the main components of coal-fired flue gas, the SO_2 removal performances of I_2/HI absorption system in the presence of NO and O_2 were investigated. As can be seen in Fig. 5, there is no distinct difference on the SO_2 removal efficiency with the increasing of NO and O_2 concentration. It is well known that the O_2 could react with HI and generate I_2. It should promote the SO_2 absorption by increasing the I_2 concentration in absorption solution. But the reaction rate between O_2 and HI is too slow to affect the SO_2 removal by I_2/HI absorption system. The NO could also be oxidized by O_2 and produce NO_2. Then, NO_2 will dissolve in water to generate HNO_3. It may inhibit the SO_2 absorption by lower the pH value of absorption solution. Nevertheless, the NO concentration in coal-fired flue gas is very low. Consequently, it will not inhibit the SO_2 removal greatly.

3.5. Multiple absorption research

The main SO_2 absorption products by I_2/HI absorption system are H_2SO_4 and HI. The concentrations of H_2SO_4 and HI will increase gradually with the continually absorption of SO_2. The accumulation of H_2SO_4 and HI may affect the SO_2 removal efficiency by I_2/HI absorption system. In order to investigate the influence of H_2SO_4 and HI accumulation in absorption solution on SO_2 removal, a hundred cycles of SO_2 absorption tests were performed. As shown in Fig. 6a, the SO_2 removal efficiency was about 67.4% after 100 runs adsorption experiments when I_2 concentration was 6.4 mmol/L. At this time, the H_2SO_4 and HI concentration were about 0.6 and 1.2 mol/L, respectively. Obviously, the SO_2 removal efficiency decreased with the accumulation of H_2SO_4 and HI. However, the SO_2 removal efficiency increased to 80.2% when the I_2 concentration increased to 25.6 mmol/L. The SO_2 removal efficiency was better when the I_2 concentration was higher (Fig. 6b). That meant the SO_2 removal efficiency could be improved by increasing the I_2 concentration.
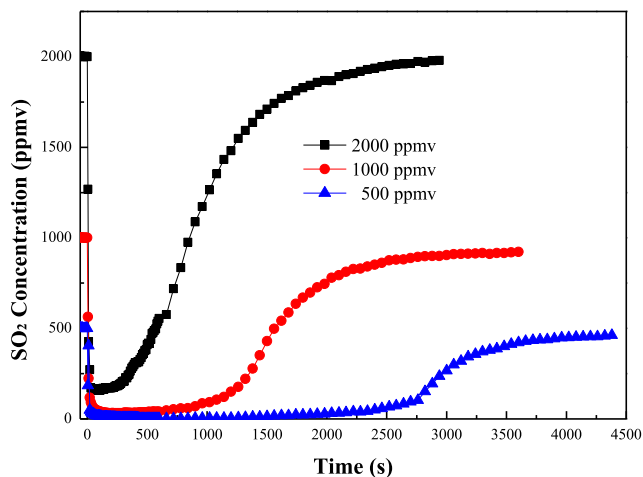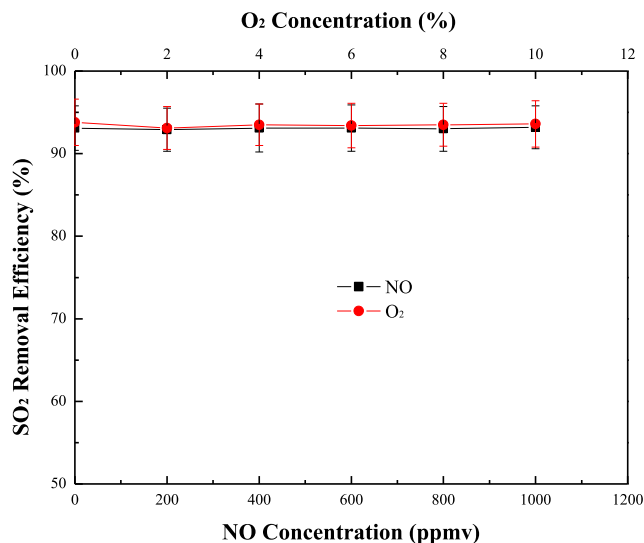

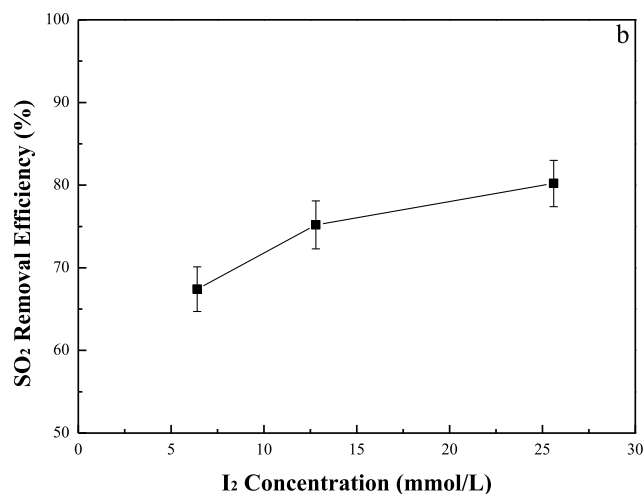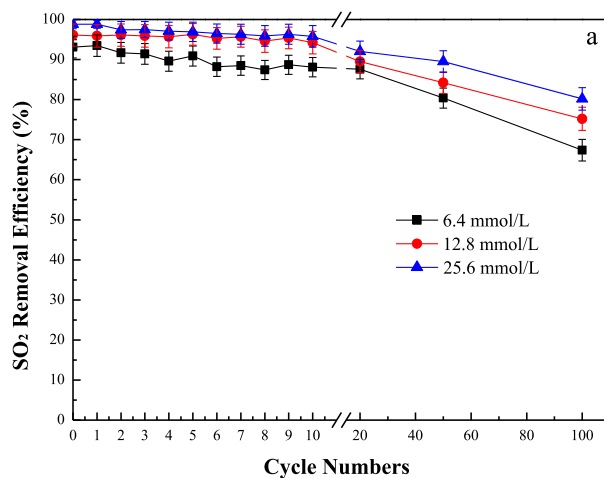**Fig. 5.** The influence of flue gas components on the SO_2 removal.

Fig. 6. The influences of cycle numbers and I_2 concentration on the SO_2 removal.

3.6. The separation of FGD byproducts

The separation of FGD byproducts is important for the industrial application of I_2/HI absorption system. The main products should be separated easily because the boiling points of H_2SO_4 and HI are different. So, the practicability of FGD byproducts separation

Fig. 4. The SO_2 absorption curve under different initial SO_2 concentration.

Table 1
The HI and H_2SO_4 concentration in the separation sample of absorption solution.

Sample	Volume (mL)	I^- concentration (mmol/L)	SO_4^{2-} concentration (mmol/L)
Original solution	50	89.7	10.6
Distilled solution	46	68.5	0.1
Residual solution	4	331.0	130.4

by distillation was investigated. The absorption solution was distillated at 408 K for 2 h, and the distilled solution and residual solution were detected by UV spectrophotometer, respectively (Fig. A3). As shown in Table 1, the SO_4^{2-} and I^- concentration in distilled solution (46 mL) were about 0.1 mmol/L and 68.5 mmol/L, respectively. It meant about 99.1% H_2SO_4 was separated from the original absorption solution to the residual solution and 70% HI was separated to distilled solution. Therefore, the adsorption products could be preliminarily separated from the absorption solution by distillation.

4. Conclusions

A new wet FGD method based on Bunsen reaction was investigated in this paper. SO_2 could be removed efficiently in I_2/HI absorption system. The SO_2 removal efficiency of I_2/HI absorption system is over 98.8% and close to that of the traditional limestone FGD process or sodium alkali scrubbing process. There is no obvious effect on SO_2 by the main coal-fired flue gas components. The main FGD byproducts are H_2SO_4 and HI, which could be separated by distillation. The energy needed in distillation could be provided by the waste heat from the coal combustion, which will save the running cost greatly. H_2SO_4 has better market prospect than traditional wet FGD products, such as gypsum, magnesium sulfate or ammonia sulfate. Moreover, HI could be decomposed to H_2 and I_2. H_2 is a clean energy and I_2 could be used to absorb SO_2 from flue gas again. Compare with the traditional wet FGD system, there is no extra energy needed to support the new absorption system. In short, this method represents a promising and economical technology for the removal and reclamation of SO_2 from the coal-fired flue gas.

Acknowledgment

Appendix A. Supplementary material

The Ion Chromatography and UV spectrophotometer of absorption products are in the Appendix.

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2017.01.045.

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