

# Effect of coal ash on hydrazine degradation under stirring and ultrasonic irradiation conditions

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## Abstract

The degradation of hydrazine ( $N_2H_4$ ) with concentrations of 0.1–5.0 mmol/L was investigated as a function of amount of coal ash (0.0–5.0 wt%) under the stirring (300 rpm) and ultrasonic irradiation (200 kHz, 200 W) conditions. It was found that the rate of decrease in the hydrazine concentration depended upon an amount of coal ash under the stirring and ultrasonic irradiation condition. It was considered under the stirring condition that hydrazine was adsorbed and degraded partly on coal ash. Furthermore, the sonochemically formed OH radicals were more effective in the hydrazine degradation than stirring condition in the presence of an intermediate amount of coal ash (0.6–2.4 wt%), whereas the effect of OH radicals disappeared in the presence of coal ash more than 2.4 wt%.  
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## 1. Introduction

The amount of hydrazine ( $N_2H_4$ ) produced in Japan in 1997–2001 has been reported to be in a range from 15,000 to 19,000 ton per year [1]. Hydrazine is used as deoxidant to remove dissolved oxygen from boiler water in thermal power stations, and is used as fuel for many rockets and spacecraft. However, it is known that hydrazine injures lungs, liver, kidney, and central nervous system [2]. In addition, the International Agency for Research on Cancer (IARC) has claimed that hydrazine is possible to be carcinogenic to humans. At present, the degradation of hydrazine is generally conducted by using oxidizing agents such as sodium hypochlorite (NaOCl) [3]. On the other hand, since wastewater regulations of thermal power stations are increasingly strengthened, reduction of chemicals such as NaOCl for wastewater treatment is also demanded [4].

The application of ultrasound to the degradation of environment pollutants in water has been reported: for example, polycyclic aromatic hydrocarbons [5], hydrogen sulfide [6], chlorinated hydrocarbons [7,8] and diverse phenols [9,10]. It has been reported that the chemical effects of ultrasound result from the phenomenon of acoustic cavitation [6,11].

Recently, Keck and coworkers have reported the formation of hydrogen peroxide and elimination of aromatic compounds in the presence of quartz particles [12]. They have suggested that the yield of the oxidation of organic compounds is enhanced by the addition of quartz particles under ultrasonic irradiation condition. Sekiguchi and coworker have reported the effects of amount, diameter and surface area of alumina particles on the sonochemical degradation of chlorobenzene [13]. They have suggested that the degradation rate is proportional to the surface area of particles, and the mechanisms were discussed including the increase in the number of cavitation bubbles. Tuziuti and coworkers have studied the correlation between acoustic cavitation noise and enhancement of a sonochemical reaction in the presence of alumina particles [14]. They

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have reported that the enhancement in the yield of sonochemical reaction by appropriate particle addition comes from an increase in the number of cavitation bubbles.

Coal ash produced from a thermal power station is composed of inorganic oxides such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ , etc., and is mainly used as cement or concrete materials. However, it may be considered that the coal ash consisting of the inorganic oxides serves as a catalyst or accelerating material for the degradation of the environment pollutants and aqueous organic compounds. Recently, we found that sonochemical degradation of phenol is accelerated by the addition of coal ash [15]. In this study, we have investigated the effect of coal ash on the hydrazine degradation.

## 2. Experimental

### 2.1. Materials and sample solutions

The coal ash used here was a clinker ash produced from the thermal power station where an Australian coal was used as a fuel. The coal ash was sieved to obtain small particles in a size range of 53–106  $\mu\text{m}$ . The coal ash was composed of  $\text{SiO}_2$ : 62.0 wt%,  $\text{Al}_2\text{O}_3$ : 21.2 wt%,  $\text{Fe}_2\text{O}_3$ : 3.9 wt%,  $\text{CaO}$ : 2.0 wt% and the others such as  $\text{MgO}$ ,  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  (less than 1.0 wt%). The specific surface area of the coal ash was 5.74  $\text{m}^2/\text{g}$ , which area was measured by an automatic specific surface area and pore size distribution measuring apparatus (BEL Japan BELSORP-mini).

A sample solution with a hydrazine concentration of 0.1–5.0 mmol/L was used. The initial pH of the solutions was in the range of 8–9.

All reagent grade chemicals were purchased from Wako Pure Chemical Industries, Ltd. and used without further purification. The water purified by an Organo Purelite PRB-002A was used (resistivity  $>10^7 \Omega \text{ cm}$ ).

### 2.2. Apparatus

The experimental ultrasonic apparatus consisted of a multi-wave ultrasonic generator (Kaijo 4021, Lot. No. 54H5) with a barium titanate oscillator (Kaijo 4611, Lot. No. 68J3) of 65 mm in diameter operated at 200 kHz with an input electric power of up to 200 W. Hydrazine solution (100 mL) was sonicated in a cylindrical glass vessel of 50 mm in diameter with a total volume of 180 mL. The bottom of the vessel was planar and made as thin as possible (1 mm), because transmission of ultrasonic waves increases with decreasing the thickness of the bottom. The vessel was mounted at a constant position relative to a nodal plane of the sound wave (3.8 mm: a half of wavelength from the oscillator), and immersed into the water bath, which was cooled by an external cooler (Shibata C-305) and kept at a constant temperature of 20 °C.

Stirring experiments were carried out using a magnetic stirrer (AS ONE DP-1 S) with a stirring bar (40 mm). The stirring speed was 300 revolutions per minute (rpm).

### 2.3. Analysis

The concentrations of hydrazine and ammonium ion were determined by the *p*-dimethylaminobenzaldehyde and the indophenol blue analytical methods based on Japanese Industrial Standards [16] with a Hitachi spectrophotometer U-2800, where absorption intensities at 458 nm and 630 nm were measured, respectively.

## 3. Results

### 3.1. Hydrazine adsorption and degradation under stirring condition

#### 3.1.1. Effect of coal ash under stirring condition

The effect of coal ash on hydrazine degradation was investigated under the stirring condition. Fig. 1 shows the residual hydrazine concentration as a function of stirring time in the presence and absence of coal ash (0.5 wt%) in the solutions with various initial hydrazine concentrations (0.1–1.0 mmol/L). In the absence of coal ash, the residual hydrazine concentration little changed at any initial concentrations. On the other hand, in the presence of coal ash, the residual hydrazine concentration decreased with increase in the stirring time at any initial concentrations. It was found that ammonium ions were detected in the solution after stirring, and the ratio of the transformation from  $\text{N}_2\text{H}_4$  to  $\text{NH}_3$  was estimated to be 3–7% of each initial hydrazine concentration. It is generally known that hydrazine degrade to ammonia and nitrogen as below [17]



From these results, it was considered that the initial hydrazine concentration decreased predominantly by the adsorption on coal ash and a part of the adsorbed hydrazine was degraded to ammonia and nitrogen.

Fig. 2 shows the half-value period of concentration of hydrazine as a function of initial concentration under stirring condition with coal ash (0.5 wt%). Here, the half-value period is the time required for the adsorption and degradation to be reduced to one half of its initial concentration.

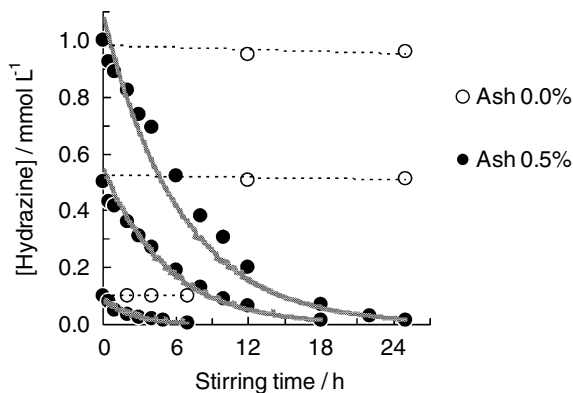


Fig. 1. The change in residual hydrazine concentration as a function of stirring time in the solutions with various concentrations.

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