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An investigation on the modelling of kinetics of thermal decomposition of hazardous mercury wastes

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HIGHLIGHTS

- A reaction mechanism of thermal treatment of hazardous mercury waste is postulated.
- The kinetic model for the thermal decomposition of mercury solid waste is deduced.
- A methodology to investigate reaction order models in solid systems is proposed.
- The thermal decomposition of mercury waste is described by two modelling approaches.

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ABSTRACT

The kinetics of mercury removal from solid wastes generated by chlor-alkali plants were studied. The reaction order and model-free method with an isoconversional approach were used to estimate the kinetic parameters and reaction mechanism that apply to the thermal decomposition of hazardous mercury wastes. As a first approach to the understanding of thermal decomposition for this type of systems (poly-disperse and multi-component), a novel scheme of six reactions was proposed to represent the behaviour of mercury compounds in the solid matrix during the treatment. An integration-optimization algorithm was used in the screening of nine mechanistic models to develop kinetic expressions that best describe the process. The kinetic parameters were calculated by fitting each of these models to the experimental data. It was demonstrated that the D_1-diffusion mechanism appeared to govern the process at 250 °C and high residence times, whereas at 450 °C a combination of the diffusion mechanism (D_1) and the third order reaction mechanism (F_3) fitted the kinetics of the conversions. The developed models can be applied in engineering calculations to dimension the installations and determine the optimal conditions to treat a mercury containing sludge.

1. Introduction

Mercury represents a huge environmental threat because it is highly toxic and persistent. It bio-accumulates and can cause neurological damage [1]. Anthropogenic emissions of mercury are causing a general increase in mercury pollution at local, regional and global scales [2]. The three largest secondary sources of mercury anthropogenic emissions include artisanal and small-scale gold mining, the production of vinyl chloride where mercuric chloride is used as catalyst, and the chlor-alkali industry [3,4].

The amount of mercury in wastes produced by chlor-alkali plants in 1995 was estimated (EU-15+Switzerland) to amount at about 95.2 tonne based on 14–17 g Hg/tonne Cl_2 capacity, only in the EU [5]. In 2000, the chlor-alkali industry was responsible for about 17% of the total anthropogenic mercury emissions in Europe with a total impact of 40.4 tonne/y [6].

Over the last decades, increased awareness of the negative impact of mercury for the environment and human health has led to stronger regulations for its emissions. Mercury cell chlor-alkali plants are not any more considered good industrial practice. The Integrated Pollution Prevention and Control (IPPC) of the European Union has indicated that chlor-alkali installations are required to obtain licenses based on the Best Available Techniques.

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Table 1
Extractants and mercury fractions defined in the sequential extraction procedure.

Fraction ID	Extractant	Extractant (ml):waste (g) ratio	Hg fraction
F1	Deionized water	20:2	Water soluble
F2	0.5 mol/l NH_4–EDTA (pH 8.4)	20:2	Exchangeable
F3	0.2 M NaOH and 4% CH_3COOH	20:2	Organic
F4	10 ml $HNO_{3\,conct}$ and 15 ml $H_2SO_{4\,conct}$	25:0.5	Residual

In the United States, only five mercury plants were kept in operation by late 2008. In Europe in 2006, mercury cells accounted for 43% of the mounted capacity. Western European producers have been committed to closing or converting all remaining chlor-alkali mercury plants by 2020 [7]. Although the technology is being phased out, the potential risk represented by thousands of tonnes of mercury wastes generated by this process will remain for a long period of time.

Cuba as a developing country still uses mercury cell technology to produce gaseous chlorine and caustic soda. It currently hosts more than 7000 tonnes of mercury contaminated wastes buried in concrete niches. Mercury wastes generated by the electrochemical Cuban plant were characterized as 'high mercury waste' (total Hg content exceeding 260 mg/kg) according to the US Land Disposal Restrictions [8]. According to USEPA [9], thermal treatment represents the most suitable technology for 'high mercury wastes'. The potential of this approach to decontaminate the mercury containing wastes from the chlor-alkali industry in Cuba has been investigated in a previous contribution [10].

Despite the fact that thermal treatment, in particular by retorting, is a widely used technology to treat solid wastes with high content of mercury (e.g. mercury wastes from the chlor-alkali process), almost all studies have focused on optimizing operating conditions at pilot and industrial scale [11–15]. Very few studies have been published on reaction mechanisms that may represent mercury behaviour during the thermal treatment [16]. On the other hand, several kinetic models exist for homogeneous mercury reactions in the gas phase. Most of these studies have been dedicated to unravel the reaction mechanisms of mercury oxidation, specifically in the context of exhaust gases emitted from coal-fired power plants [17–27]. An elementary reaction mechanism for homogeneous Hg^0 oxidation with an emphasis on major interactions among Cl-species and other pollutants in coal derived exhausts has been proposed and evaluated [21]. The kinetic mechanism of mercury oxidation, by ab initio calculations of quantum chemistry, has been studied and the rate constant calculated using the transition state theory [24]. Recently, the rate constants for the 8-step homogeneous Hg–Cl reaction mechanism that describes mercury oxidation in combustion systems have been determined using the transition state theory [26].

Heterogeneous mercury reactions have been less studied. Only thermal decomposition of mercury oxide seems to play an important role in the knowledge of the mercury solid phase reactions [27]. The kinetic and thermal decomposition of HgO was studied and a dissociative evaporation scheme that includes two different HgO(s) reactions at high (<650 K) and low decomposition temperature was developed [27]. Moreover, an investigation of the retardation effect of oxygen on the evaporation rate of HgO concluded that the dissociative evaporation of HgO proceeds with the release of atomic oxygen as a primary product of decomposition [28]. Nevertheless, based on a literature survey, there are no kinetic and thermodynamic studies about the mechanism of mercury removal from solid wastes generated in chlor-alkali industries during thermal decomposition which includes homogeneous and heterogeneous reactions for mercury contaminated wastes generated by chlor-alkali industries.

This paper intends to elucidate the kinetics of the mercury removal from solid wastes by thermal decomposition using two different approaches, a model-free based on a differential isoconversional approach and reaction order methods. Moreover, as a first depth into the knowledge of thermal decomposition for this type of systems (poly-disperse and multi-component), this communication aims to obtain the reaction pattern and the thermodynamic feasibility of the studied system considering both homogeneous and heterogeneous reactions.

2. Experimental

2.1. Sampling and chemical analysis

The mercurial sludge sample used for the experiments was collected from a filled niche, located around the Cuban chlor-alkali production facility "ELQUIM". The procedures applied to sampling, sample preparation and chemical analysis have been described in a previous paper [10].

2.2. Mercury fractionation

Fractionation by using a sequential extraction constitutes an operationally defined procedure that allows to identify various classes of species of an element and to determine the sum of its concentrations in each class [30].

The fractionation of Hg was performed according to the four step procedure outlined by Neculita et al. [31] (Table 1).

The extraction was performed using 2 g of accurately weighted sample mixed with 20 ml of solvent in a 100 ml centrifuge tube. The tubes were thoroughly shaken for 2 h at $20 \pm 2\,^\circ C$ using an end over end shaker operating at about 30 rpm. Between each extraction and rinse step, the supernatant was obtained by centrifuging at 3000 rpm for 15 min at $10\,^\circ C$ followed by filtration using 0.45 μm pore membrane filters. The rinsing steps consisted of washing the leached residues twice with deionised water (20 and 10 ml) during 15 min. Rinses were always subsequently added to the solvent extract from the same sample. The resulting combined supernatant from the first three extraction steps was analyzed for total Hg content by CVAAS. Residual Hg was extracted by adding the same reagents as for total Hg determination in the waste sample directly in the original 100 ml centrifuge tube. The sample was then transferred into a 100 ml standard volumetric flask. The digestion was performed using the same procedure as previously described for total Hg in the waste sample [10].

2.3. Thermal treatment

The thermal decomposition technology of these mercury wastes, which is based on volatilization and subsequent condensation of the mercury vapours, results in the recovery of metallic mercury [13,32].

The thermal treatment of the mercurial sludge was performed at laboratory scale using a ceramic muffle furnace (L9/11/SKM/P330 Model, Nabertherm, Germany, Bremen) which has a temperature control accuracy of $\pm 1\,^\circ C$. The oven was placed inside a fume