

Gas-solid reactions for the removal of hydrogen halides: a critical review in the light of novel challenges in flue gas cleaning applications

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Highlights

- Experimental data on hydrogen halides removal by different sources were systematized
- Reactivity trends as a function of sorbent, halide and operating conditions were reconstructed
- Open issues in the modelling of gas-solid reactions for acid gas removal are discussed
- Studies on HF, HBr and on simultaneous sorption of halides are identified as research priorities

1. Introduction

Hydrogen halides (HCl, HF, HBr) are typical acid pollutants generated by combustion processes, in several industrial sectors (cement, iron and steel, ceramics and glass manufacturing), in conventional waste-to-energy (waste incineration of urban and industrial waste) and in novel thermal recycling processes of selected waste fractions (e.g., the thermal treatment of electronic waste and lithium-ion batteries).

Although the removal of hydrogen halides from flue gases via dry sorbent injection has been performed in industry for more than 30 years, the operation of such abatement systems has been mainly empirical, relying on large excess of reactant feeds to ensure wide safety margins in complying with emission standards. Nowadays, emission standards on acid gases imposed in environmental permitting are becoming increasingly stringent, in line with the ambitious EU “Zero Pollution” Action Plan. At the same time, in a holistic approach towards environmental protection, operators are often required to minimize the indirect impacts of dry sorbent injection, i.e., the production of reactants and the generation of solid residues. Therefore, interest for the optimization of the acid gas removal process is surging but, despite the apparent simplicity of the related gas-solid reaction processes, several fundamental aspects are still obscure.

As a preliminary step of an experimental program by LISES@UNIBO on dry acid gas treatment, a systematic review on gas-solid reaction processes for the removal of hydrogen halides with Ca-, Na-, and Mg-based sorbents has been conducted. The review was aimed at collecting and systematizing the relatively fragmented literature on the topic to: i) combine experimental evidences from different sources to reconstruct reaction data on the widest combinations of hydrogen halides, sorbents, and operating conditions (temperature, humidity, flue gas composition), ii) analyze the open issues in the phenomenological characterization of the reaction process and the modelling approaches adopted to target them, and iii) identify the key gaps that ongoing research in the field should aim to address.

2. Methods

Scientific publications of relevance for the review were collected using a set of representative keywords (and combinations thereof). Experimental data on acid gas sorption (breakthrough curves and sorbent conversion data), typically reported as plots by authors, were digitized, harmonized in terms of unit of measurement, and time series were normalized according to the acid gas-to-sorbent ratio adopted by authors, in order to allow cross-comparison between different studies.

3. Results and discussion

Figure 1 summarizes the structure of the review study and the related aims.

For aim 1, reaction data retrieved in literature were classified, compared and combined. For instance, by putting together data of the reaction between HCl and Ca(OH)₂ from separate studies that focused on relatively narrow temperature intervals, it was possible to reconstruct the evolution of the reactivity of the sorbent across the entire range from room temperature up to over 1000 °C and to better quantify how it is affected by the interplay of different phenomena (adsorption of flue gas humidity, sintering of the sorbent, temperature effect on kinetics) at different temperatures.

For aim 2, interpretations of the governing phenomena of the reaction process were reviewed. Particular attention was given to the different approaches adopted by authors to adapt conventional models for gas-solid reactions (shrinking core and grain model or random pore model) to better model product layer growth and diffusion, the main limiting steps of the reaction process for acid gas removal. Data on the kinetic and diffusivity parameters for a wide range of experimental conditions were collected and compared to provide a suitable dataset for the integration of gas-solid reaction models into models of the acid gas removal operation at industrial scale.

For aim 3, the experimental conditions tested in literature were compared with the relevant conditions in flue gas cleaning applications of industrial interest. The study of the simultaneous sorption of multiple acid gas compounds is identified as the main area where research is needed, in order to elucidate possible synergic or competitive interactions between the acid species. Such studies should aim to include a number of acid gas species so far relatively overlooked but of increasing relevance for novel flue gas treatment applications (namely, HF and HBr).

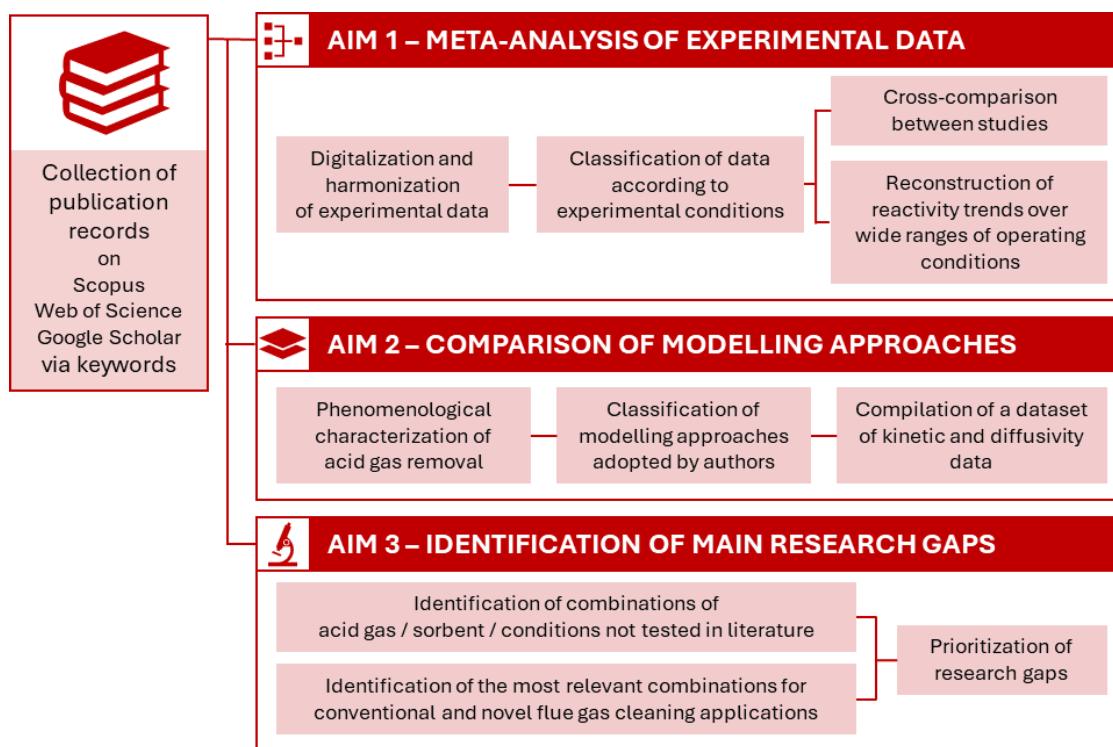


Figure 1. Overview of aim, scope and methods of the review on dry removal processes for hydrogen halides.

4. Conclusions

The present work systematized the corpus of research conducted by different authors over three decades, combining the related experimental data to present a broad characterization of the reactivity of different sorbents towards different hydrogen halides at different operating conditions. Open issues in the modelling of the fundamental phenomena of the acid gas removal reaction process were identified and discussed in the light of the different approaches so far adopted. A list of priorities of industrial relevance for this research field was put forth.

Keywords

Gas-solid reactions; acid gas removal; shrinking core; sorbents.