Supporting Materials for

Investigation of molten ZnCl2 natural particle suspensions

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Context:

PS 1: The infrared (IR) spectroscopy experiments.

PS 2: Ultraviolet-Visible (UV-Vis) spectra of natural particle suspensions (NPSs) for Cr and Fe.

PS 3: The analysis parameters for ICP-OES.

PS 1: The infrared (IR) spectroscopy experiments.

A control sample (sample A) was the cooled $ZnCl_2$ which had been melted for 3 h at 470 °C in air. After the UV-Vis spectroscopy experiments for metals at 470 °C, the natural particle suspensions (NPSs) for Cr and Fe were cooled to room-temperature and solidified salt sample containing Cr (sample B) and solidified salt sample containing Fe (sample C) were obtained.

Then, these three kinds of samples were detected by IR spectroscopy (PerkinElmer Frontier). Because $ZnCl_2$ is covalent compound with IR spectra vibration absorption peaks and IR spectra obey Beer's-type law [1, 2], it is inevitable that the vibration absorption peaks of trace insoluble substances would be very weak. Therefore, two different strategies were used to increase the signal to noise ratio (SNR) of IR spectra of sample B and sample C:

1. For sample B, the part of salts in the UV-Vis light path was detected, and the IR spectra were collected and accumulated 190 times (collection time: 5min).

2. For sample C, the part of salts (the dark-red floating matter displayed in **Fig. 2c** and **Fig. 2d** in the manuscript) at the salt-gas interface was directly detected by IR spectra.

Figure S1 shows the IR spectra of these three samples. Curves A, B and C correspond to samples A, B and C, respectively. The IR spectra of three samples at the wave number range of 500-1100 cm^{-1} are displayed in **Fig. S1a**, which were directly detected (collected and accumulated only 5 times). Those 8 vibration bands, which are detected on all three curves and located at 550, 598, 760, 792, 847, 925, 952 and 960 cm^{-1}, belong to molten $ZnCl_2$. On curve C in **Fig. S1a**, extra shoulders at wave number near 892, 650, 620 and 545 cm^{-1} appear. On curve B in Fig. S1a, there were no extra shoulders or peaks. **Fig. S1b** displays the IR spectra of sample A and sample B at the wave number range of 565-650 cm^{-1}, which were collected and accumulated ~190 times (collection time: 5 min). On curve B in **Fig. S1b**, two obvious extra vibration peaks located at 575 and 625 cm^{-1} appeared.

The extra shoulders on curve C (**Fig. S1a**) suggested the main composition of corrosion products in NPSs for Fe is Fe_2O_3 [3, 4]. The extra peaks on curve B (**Fig. S1b**) characterizes the Cr_2O_3 phase [5]. Because the element Cr concentration in the NPSs for Cr was less than 150 mg/kg (see **Fig. 5a** in the manuscript), there were no extra shoulders or peaks for chromium compounds could be observed on the curve B in **Fig. S1a**. When the spectra of sample B were collected and accumulated 190 times (collection time: 5 min), the SNR increased, and then two obvious extra vibration bands located at 575 and 625 cm^{-1} which characterized the Cr_2O_3 phase [5] could be observed.

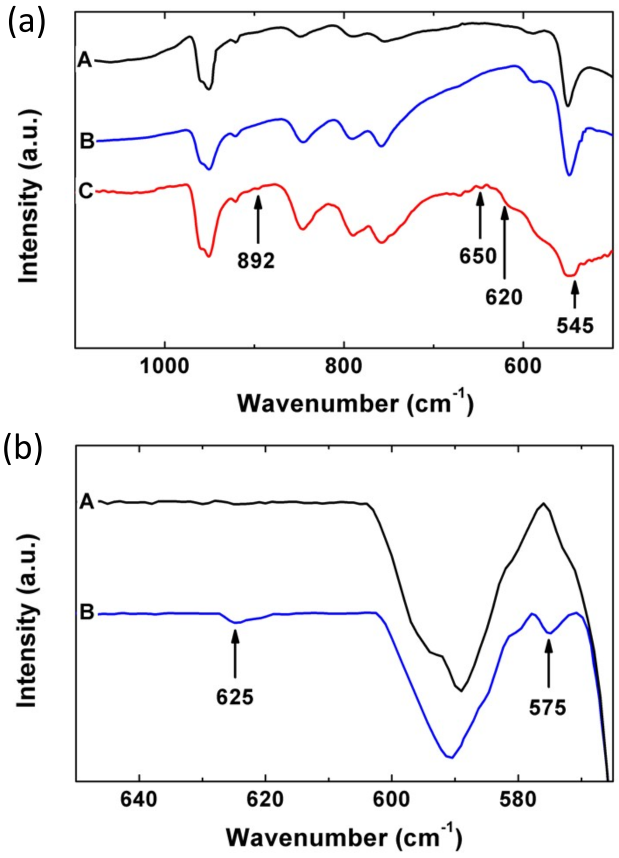

Fig. S1. Infrared (IR) spectra of control sample (curve A), solidified salt sample containing Cr (curve B) and solidified salt sample containing Fe (curve C). The IR spectra at wavenumber range of 500-1100 cm^{-1} are displayed in **(a)** and the IR spectra at wavenumber range of 565-650 cm^{-1} are displayed in **(b)**. The control sample was the cooled ZnCl2 which had been melted for 3 h at 470 °C in air. The solidified salt samples containing Cr and Fe were obtained by cooling the NPSs for Cr and Fe, which formed by the corrosion of metal Cr and Fe in molten $ZnCl_2$ for 3 h at 470 °C.

PS 2: Ultraviolet-Visible (UV-Vis) spectra of natural particle suspensions (NPSs) for Cr and Fe.

Figure S2 and **Fig. S3** are the UV-Vis spectra of NPSs for Cr and Fe, respectively, which were recorded 105 times and the time interval was 100 s. The axes of UV-Vis spectra have log scaling to exhibit the linearity of the spectra in the higher wavelength range (typically from 400 nm and up). Moreover, these spectra line slopes change only over a relatively small range.

When spectra line slopes change only over a relatively small range, according to Tyndall spectra, the particle radius *r* is approximately proportional to the spectra line slope (see equation (4) in manuscript), and based on the Beer's-type law for suspensions, A*slope* can be used to approximately present the change of concentrations of corroded metal elements (see equation (12) in manuscript). Here, A is the absorbance value of a linear fitting spectrum at the wavelength of 800 nm.

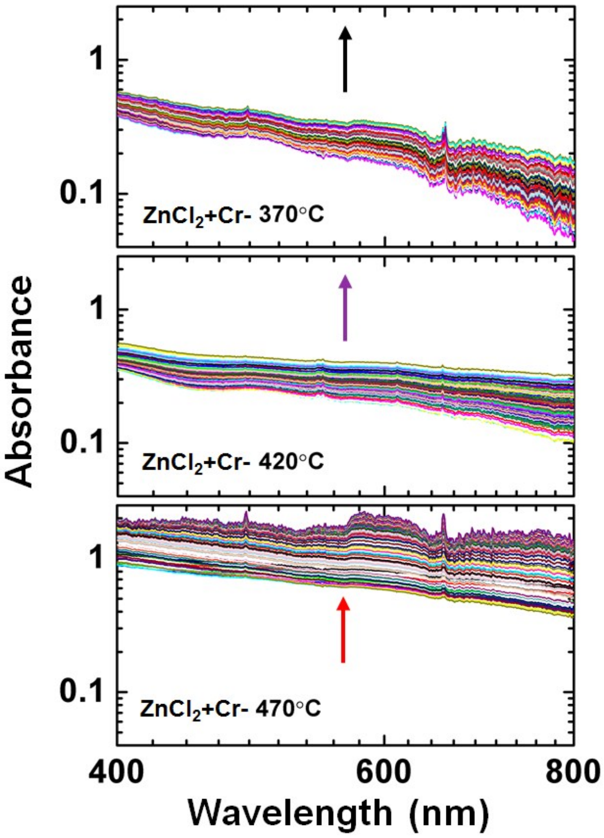

Fig. S2. The ultraviolet-visible (UV-Vis) spectra of natural particle suspensions (NPSs) for Cr. The NPSs were produced by the corrosion of metal Cr at 370, 420 and 470 °C in air. These spectra were recorded 105 times and the time interval was 100 s.

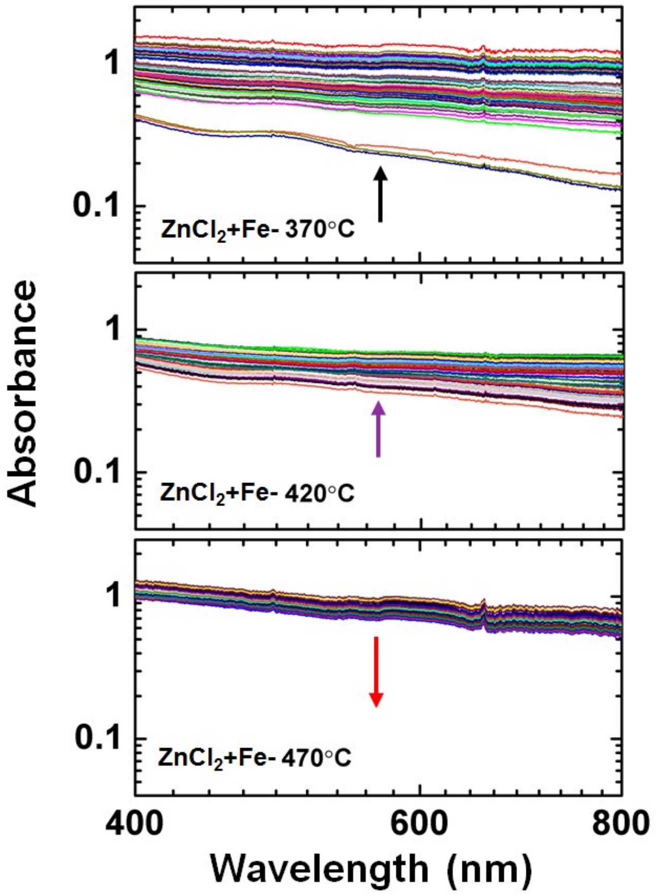

Fig. S3. The ultraviolet-visible (UV-Vis) spectra of natural particle suspensions (NPSs) for Fe. The NPSs were produced by the corrosion of metal Fe at 370, 420 and 470 °C in air. These spectra were recorded 105 times and the time interval was 100 s.

PS 3: The analysis parameters for ICP-OES.

The analysis parameters for ICP-OES are shown in **Table S1**.

Table S1 The analysis parameters for ICP-OES

Parameter	Values
Holographic grating of monochromator	3600 grooves mm^{-1}
Resolution	0.008 nm
Plasma power	1400 W
Pump speed	30 rpm
Coolant flow	12 L/min
Auxiliary flow	1.5 L/min
Nebulizer flow	1.1 L/min
Frequency	27.12 MHz
Wavelength of Cr	267.653 nm
Wavelength of Fe	238.204 nm

We collected 0.3 g solidified salt near the UV-Vis light path very carefully, grounded it into powder, divided into three equal parts, every part was dissolved in 15 ml nitric acid concentrated (~13 wt. %). The nitric acid solutions were placed in the water bath simultaneously and kept the temperature at 80 °C for 8 hours, then dilute them with deionized to 50 ml.

References

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