Mass Spectrometric Study of the Decomposition of $CoSO_4$ and $CoSO_4–Na_2SO_4$

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Marine gas turbines are attacked at 600–750 °C by molten salts which corrode the turbine blades. The principal corrodent is eutectic $CoSO_4–Na_2SO_4$, formed by reaction of SO_3 (from fuel combustion) and Na_2SO_4 (from sea salt) with cobalt oxide on the blade surface [1, 2]. We have postulated that corrosion is initiated by high local concentrations of SO_3 produced by decomposition reactions of the molten $CoSO_4–Na_2SO_4$. Recent experiments in this laboratory have shown that SO_3 is the predominant gas evolved by $CoSO_4–Na_2SO_4$ as it decomposes in air [2]. The present investigation was undertaken to determine the intrinsic gases evolved by $CoSO_4–Na_2SO_4$ as it decomposes, and to compare the gases with those evolved by decomposition of $CoSO_4$ alone.

Cobalt sulfate is described as decomposing according to reaction (1)

$$CoSO_4 \rightarrow CoO + SO_3 \quad (1)$$

or reaction (2)

$$CoSO_4 \rightarrow CoO + SO_2 + 1/2O_2 \quad (2)$$

However, there are few experimental data in the literature [3–5] to indicate which reaction prevails, or under what conditions. Furthermore, reaction (3), which is known to be catalyzed by cobalt oxide [2, 4, 6], can obscure the intrinsic decomposition products.

$$SO_3 \rightarrow SO_2 + 1/2O_2 \quad (3)$$

Sodium sulfate does not decompose perceptibly below 900 °C, even in vacuum [7].

In these experiments cobalt sulfate alone and $CoSO_4$ with Na_2SO_4 were compared. The cobalt sulfate specimens were prepared by dehydrating $CoSO_4 \cdot 7H_2O$ in vacuum at 450 °C. X-ray analysis of the dehydrated salt showed that no cobalt oxide had formed during dehydration. Some $CoSO_4 \cdot 7H_2O$ was dehydrated in the mass spectrometer where we observed that complete dehydration occurred before decomposition began. Completeness of dehydration was verified by the fact that no water peaks (above normal instrument background) were detected in the subsequent mass spectrometric analysis. The cobalt sulfate–sodium sulfate samples were prepared in two ways: by mechanically mixing and grinding 50 mole percent (m/o) $CoSO_4$ with Na_2SO_4, or by sulfating mixtures of $Co_3O_4–Na_2SO_4$ under equilibrated $SO_2–SO_3$ in air at 700 °C to produce 'melts' of $CoSO_4–Na_2SO_4$. Two specimens, the 30 and 33 m/o melts listed in Table 1, were produced by the latter method. The 30 m/o melt contained 7 m/o excess Co_3O_4, while the 33 m/o melt contained less than 1 m/o Co_3O_4. The mechanically mixed $CoSO_4–Na_2SO_4$ was prepared by mixing $CoSO_4 \cdot 7H_2O$ and dehydrating the mixture at 450° in vacuum, or by mixing previously dehydrated $CoSO_4$ with Na_2SO_4. The drying technique did not affect the mass spectrometer results.

The decomposition of the salts was examined at 700 °C in vacuum in a high temperature mass spectrometer previously described [7]. Samples of about 1 gm for the $CoSO_4$ and mechanically mixed $CoSO_4–Na_2SO_4$, and about 100 mg for the $CoSO_4–Na_2SO_4$ melts, were tested in open alumina crucibles. An ionization energy of 17 eV was used to minimize fragmentation of the gases in the mass spectrometer [8]. The peak heights were constant during measurement (0.5–1 hr at temperature). There was no mass spectrometric evidence of Na_2SO_4 decomposition, such as Na^+. X-ray diffraction of the residue confirmed that CoO was produced by decomposition of both the $CoSO_4$ and $CoSO_4–Na_2SO_4$. The high temperature form of $Na_2Co(SO_4)_2$ was also identified by X-ray diffraction in the $CoSO_4–Na_2SO_4$ specimens.

The results compiled in Table I show that the ratio of peak heights of SO_3 to SO_2 are much higher (~100X) for the $CoSO_4–Na_2SO_4$ specimens than for $CoSO_4$. The very low SO_3 to SO_2 peak ratio for $CoSO_4$ decomposition suggests that reaction (2) predominates in this case. This is contrary to Knittel *et al.* [6] who found that sulfates decomposing in the same temperature range as $CoSO_4$ ($ZnSO_4$, $CuSO_4$ and $Al_2(SO_4)_3$) released only SO_3; that is, decomposed by reaction (1). Presumably cobalt sulfate could decompose via reaction (1) with all the SO_3 transformed to SO_2 and O_2 by CoO catalysis of reaction (3). However, this reaction path seems unlikely, since no SO_3 to SO_2 transformation was observed in a similar decomposition where a catalytic oxide was produced (*i.e.*, CuO in $CuSO_4$ decomposition [6]).

In contrast to $CoSO_4$, the $CoSO_4–Na_2SO_4$ specimens all evolved SO_3, and in higher proportion as the $CoSO_4$ content increased (Table I). However, there is also a substantial output of SO_2 and O_2. Although present experiments can not prove which, we assume that either the $CoSO_4–Na_2SO_4$ molten mixtures decompose *via* reactions (1) and (2) simultaneously; or that reaction (1) occurs first, followed by partial SO_3 transformation by reaction (3).

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TABLE I. Ratio of SO_3 to SO_2 Peak Intensities[a] in the Decomposition of Sulfates at 700 °C in Vacuum.

$CoSO_4$		$CoSO_4-Na_2SO_4$			
Run 1	Run 2	50 m/o mixture		33 m/o melt	30 m/o melt
		Run 1	Run 2		
0.0017	0.0067	0.45	0.45	0.35	0.24

[a] Uncorrected for sensitivity of mass spectrometer to each ion and thus not directly representative of the gas partial pressures.

Cobalt sulfate alone may decompose differently than $CoSO_4$ and Na_2SO_4 mixtures because at 700 °C $CoSO_4$ is a solid whereas the $CoSO_4-Na_2SO_4$ mixtures are molten. The environment of the sulfate anion would be quite different in a liquid compared to a solid in terms of steric factors, polarization, and freedom of movement; hence the release of SO_3 is possibly promoted from a liquid. Alternatively, it could be considered that $CoSO_4$ decomposes to SO_2 and O_2 (that is, with all SO_3 being transformed by CoO catalysis) in the solid but not in the melt, because CoO is a less effective catalyst in the melt than when in contact with solid $CoSO_4$. The catalytic activity of CoO is believed to be related to its properties as a p-type semiconductor [6] which may be obscured when CoO is present in molten $CoSO_4-Na_2SO_4$.

Although the mechanisms remain unexplained, these experiments confirm that SO_3 (along with SO_2 and O_2) is evolved from molten $CoSO_4-Na_2SO_4$ in vacuum at 700 °C, while $CoSO_4$ alone decomposes to release only SO_2 and O_2.

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