LOCATION AND ASSIGNMENT OF ALL SPIN ALLOWED AND FORBIDDEN BANDS OF Ni(II), Cr(III) AND Fe(III) COMPLEXES IN FUSED (Na,K,Al)(SO$_4$,Cl)

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ABSTRACT

Our first contribution described a new spectroscopic technique for measuring hot corrosion: this contribution shows how computer treatment of the digitised spectra therein recorded can yield considerable information concerning the corrosion products, transition metal complex ions, dissolved in the molten salts. The spectra of nickel(II), chromium(III) and iron(III) in the system (Na,K,Al)SO$_4$ with added chloride between 560 and 740°C were recorded, and their second and fourth differentials carefully computed by various methods, with total consistency. Consequently all the spin-allowed and spin-forbidden bands (and no more) were assigned, and the geometries, basically octahedral or tetrahedral, of the transition metal complex ions were identified. Many of the spin-forbidden bands, particularly for Fe(III) complexes, have not previously been located. Chloride was added, to study its effects, because coals with higher than usual chlorine content are becoming available, and hot corrosion generally increases markedly with only small increases in chlorine content.

INTRODUCTION

Once a spectrum has been digitised a number of mathematical manipulations and analyses can be performed in a mainframe computer. Two such processes, smoothing and resolution by higher derivative analysis will be first discussed, and then the results of these treatments on the spectra of nickel(II), chromium(III) and iron(III) in
molten (Na,K,Al)SO₄ with added chloride will be given and discussed in terms of the transitions assigned and the geometries of the various complex ions identified. This fundamental study was initiated because coal from new coalfields, with higher-than-average chlorine content, is expected to increase significantly the rate of hot corrosion.

SMOOTHING OF SPECTRA

Pen noise is inherent in all spectral measurements. Although it cannot be eliminated, it is possible to reduce noise by a number of methods.

Experimentally, noise can best be reduced by taking the average of a number of recordings of a particular spectrum. This method is both time-consuming and inappropriate when dealing with samples which change with time or are not stable over long time periods. Furthermore, improvement in the signal-to-noise (S/N) ratio increases only with the square root of the number of spectra averaged.

Mathematical smoothing may be applied to digitised spectra. Methods involving a simple moving average, or non-linear triangular and exponential smoothing functions have been discussed by Savitzky and Golay (1). Such methods were discounted by these authors, since they lead to distortion and reduction in intensity of the peaks. Instead, Savitzky and Golay evaluated an exact least-squares method, from a procedure derived theoretically by Worthing and Geffner (2). This method involves the fitting of a polynomial, of degree n (n = 2 to 6), to an array of data points, recorded at equal sampling intervals, to obtain the smoothed value for the datum point at the center of the array. The data set is then moved forward by one point, and the process repeated until the whole spectrum has been smoothed. This operation is referred to as an "x point convolute", where x = 2m + 1, and m is the number of data points preceding and following the datum point at the center of the array.

This convolution method has the advantage that it is non-iterative, and therefore requires very little computing time. The degree of noise reduction is proportional to the square root of the number of points used in the convolution. Spectra characterised by insufficient data points may suffer degradation as a result of this smoothing procedure. This is most common when large digitising intervals are used to record narrow absorption bands. The spectra in
this study were digitised at 1 nm intervals, and no degra-
dation of the broad d—d bands was observed.

The tables of convolution coefficients given by
Savitzky and Golay (1) contain a number of mistakes
resulting from an error in their reasoning. This was
noted by Steinier et al. (3), who published the corrected
coefficients. We have available a computer program that
determines from first principles the convolution coeffi-
cients for any value of x and n, the number of points in
the convolute and degree of the polynomial to be used,
respectively (4).

RESOLUTION OF SPECTRA BY HIGHER DERIVATIVE ANALYSIS

The convolution method of Savitzky and Golay (1) may
also be applied to the calculation of the derivatives of a
spectrum, by using the appropriate set of coefficients.
Indeed, smoothing should more properly be regarded as a
special case of a general method to calculate the n
th derivative of a polynomial fitted to the digitised data at
each particular point: for smoothing, n = 0, i.e. the
zeroth order derivative.

In Figure 1, the first four derivatives of a simulated
absorption profile are shown. The ordinate scales of the
plots are not comparable, and the figure does not therefore
reflect the true ratios of the peak heights. The first
derivative is of limited value for curve resolution. It is
zero at observed peak maxima (and also minima), but may be
used to locate such maxima precisely. The second and
fourth derivatives are similar in shape (the second deriva-
tive being inverted) to the original band, but much
sharper, as can be seen from Figure 1. In the case of
Gaussian bands, the second and fourth derivatives have
half-widths (i.e. the full width at half-height) which are
53 and 41%, respectively, of the original band half-width.
For a Lorentzian band, the corresponding values are 33 and
20%.

An observed spectrum is the envelope resulting from
the summation of the bands which comprise the spectrum. If
these component bands are overlapping to any significant
extent, the observed maxima will not correspond to the
positions of the maxima of the constituent bands. Indeed,
overlap may be such that no maxima are observed for one or
more of the components. The second (or fourth) derivative
of the observed spectrum is the sum of the second (or
fourth) derivative bands of the constituents. However,
because these derivative bands are sharper than the

514
originals, individual maxima will now be observed for previously unresolved combinations.

This is the basis of this resolution method. It is particularly useful when only the positions and relative intensities of the bands need to be known. It has an advantage over curve-fitting methods in that no assumptions need to be made regarding the heights, half-widths, mathematical functions (e.g. whether the bands are Gaussian, Lorentzian, or log-normal etc.), or, indeed, the number of component bands.

The other important feature concerning second and fourth differential spectra of a profile containing several bands is that the derivative of the largest and broadest band is essentially lost, the height of this band is now considerably less, often two orders of magnitude less than the derivative heights of smaller and narrower bands in the original profile. In practice, for transition metal spectra this means that, in general, charge-transfer spectra essentially disappear upon even-order differentiation, but spin-allowed transitions become clearly identified, and spin-forbidden bands now appear with approximately the same heights as the spin-allowed bands.

COMBINED SMOOTHING AND DIFFERENTIATION

Since experimental noise is magnified by the differentiation process, it is desirable to smooth spectra before differentiation. It is not necessary to carry out two separate, successive convolutions, since the two sets of convolution coefficients can be used to generate a third set, which will carry out the smoothing and differentiation simultaneously (1). This latter method was used to differentiate spectra in this study. The coefficients for this purpose we calculated using a subroutine (COEFFS) written by Dr. P. Gans, in our department (4). Thus a \((m + 1)\) point smoothing, combined with a \((n + 1)\) point differentiation results in a \((m + n + 1)\) point combined smoothing and differentiation. For best results \(n\) should equal \(m\): the best value for \(n\) needs to be determined by trial and error.

Our procedure was therefore to compare the differential spectra of a profile as \(n\) (and \(m\)) were steadily increased from around 15. A persistent pattern of a constant number of peaks always appearing at the same place soon emerged, and the optimum value for \(n\) to give maximum resolution was soon identified. All other (usually small) peaks were
therefore due to random noise. In addition, second and fourth differential spectra were compared. Good agreement between the peak positions obtained separately from the second and fourth derivatives was taken to indicate that the band in question was neither spurious nor grossly distorted from its true position.

MELT SPECTRA OF Ni(II), Cr(III) AND Fe(III): A REVIEW

There are relatively few reports in the literature of the spectra of transition metal ions in sulfate melts, and none for such ions in aluminum-containing sulfate melts. The spectra in chloride systems (including those containing AlCl₃) are more widely reported. There are, however, no reports for mixed sulfate-chloride melts.

Of the three transition metal ions in question, Ni(II) has been the most extensively studied. Johnson and Piper (5) recorded the spectrum of this ion in the (Li,Na,K)SO₄ eutectic at 550°C. They concluded that a distorted octahedral nickel complex was formed, and suggested that three bidentate sulfate ligands were present in the complex. Duffy et al. (6,7) compared the spectra of Ni(II) in the (Li,Na,K)SO₄ melt, concentrated H₂SO₄, K₂SO₄-ZnSO₄ and (Na,K)HSO₄ glasses, and molten (Na,K)HSO₄. They found essentially octahedral coordination in all cases, but distinguished between bidentate sulfate and ligands in (Li,Na,K)SO₄ and monodentate sulfates in concentrated H₂SO₄ and (Na,K)HSO₄ glass. The K₂SO₄-ZnSO₄ glass containing nickel(II) has also been investigated by Narasimham and Rao (8), and again octahedral coordination was found over the entire composition range.

Chlorides generally form lower melting mixtures than sulfates, and so much more work has been performed on chlorides. Boston and Smith (9) originally studied the spectrum of nickel(II) in the (Li,K)Cl melt, and found it temperature and composition dependent, and with at least two species present. Gruen and McBeth (10) observed tetrahedral NiCl₂⁻ complexes in fused pyridinium chloride, CsCl, and in Cs₂ZnCl₄ crystals: spectra obtained in fused LiCl were thought to result from tetragonally distorted NiCl₂⁻ species.

Øye and Gruen (11) investigated nickel(II) in molten AlCl₃ at 227°C: octahedral coordination was identified. The spectrum of nickel(II) in a ZnCl₂-KCl mixture has been examined (12) over the whole composition range, and between 250 and 900°C. A two-species equilibrium was found, between octahedral and distorted tetrahedral symmetries. High
temperatures favored the four-fold coordination, while octahedral complexes were favored by high zinc content.

Brynestad et al. (13-16) have studied nickel(II) in a wide range of melts. In the (Li,K)Cl system, with temperatures in the range 363-1070°C, an equilibrium between tetrahedral and octahedral species was observed, in which the tetrahedral form was favored by increasing temperature and KCl content. The outer shell of the tetrahedral complex was thought to be principally of K+ ions, while that of the octahedral form contained largely Li+ ions. Similar behaviour was found when lithium was replaced by magnesium, in the KCl-MgCl2 system. In the CsCl-ZnCl2 system, however, distorted tetrahedral nickel(II) species were identified for a ZnCl2 content of 50 mol %. As the ZnCl2 content was increased, conversion to octahedral coordination took place, and was virtually complete beyond 72 mol % ZnCl2. The nickel ions in this complex were thought to be incorporated in a chlorozincate polymer network. In molten CsAlCl4, the chloride ion concentration is dependent on the equilibrium

\[ 2\text{AlCl}_4^- \rightleftharpoons \text{Cl}^- + \text{Al}_2\text{Cl}_7^- \]

and can be increased or reduced by adding CsCl or Al2Cl6, respectively. In a melt containing a substantial excess of chloride ions, NiCl42- was formed. A reduction in chloride ion concentration, or temperature increase, resulted in the progressive replacement of NiCl42- by a second chloronickel complex. Although this complex was not identified, its spectrum indicated that it approximated to neither octahedral nor tetrahedral symmetry.

Turning to chromium(III) in molten salts, we find very much less reported work. Johnson et al. (17) recorded the chromium(III) spectrum in the (Li,Na,K)SO4 melt at 600°C. This indicated an octahedral species, which they proposed as Cr(SO4)33-, with three bidentate sulfate ligands. The Cr(III) spectrum in the (Li,K)Cl eutectic was recorded by Harrington and Sundheim (18), who noted slight changes on increasing the temperature from 392 to 444°C. The CrCl63- species was proposed, and the observed changes attributed to thermal perturbations. Gruen and McBeth (19) also examined this system, and extended the temperature range to 1000°C. Even at the highest temperature the spectrum could still be interpreted on the basis of CrCl63- octahedra, with no indication of an octahedral-tetrahedral equilibrium.

Iron(III) is a d5 ion and thus d—d transitions are both Laporte and spin-forbidden. Consequently, the bands are very weak, and their observation is further limited by a very strong charge transfer edge which dominates the
iron(III) spectrum in molten systems. There are no reported spectra of iron(III) in sulfate melts. Harrington and Sundheim (88) obtained the spectrum in the (Li,K)Cl eutectic. It comprised a strongly absorbing shoulder below 400 nm on the side of an edge rising sharply at approximately 250 nm. An increase in temperature caused the shoulder to diminish. Comparison of this spectrum with others of iron(III) in a variety of non-aqueous solvents led the authors to propose a tetrahedral FeCl₄⁻ species. Silcox and Haendler (20) recorded the uv spectrum of iron(III) in the NaCl-KCl-MgCl₂ eutectic at 430°C. Again, a rising absorption edge was found, but this time containing possible indications of weak bands. No identification of the iron(III) species was attempted.

Although no studies have been made for mixed sulfate-chloride systems a spectrophotometric study of nickel(II) in mixed nitrate-chloride melts (21) identified various chloro-nitrato nickel(II) complexes, and an octahedral-tetrahedral equilibrium, and indicated appropriate approaches.

**EXPERIMENTAL**

Spectra were recorded on an Applied Physics Cary 14 H spectrophotometer. No modifications were made to the optics for this study and a conventional isothermal furnace was employed. It was not possible to prepare a melt of given chloride content and investigate the temperature variation of the spectrum, since Al₂Cl₆ was continually lost from the melt, and significant composition changes would have occurred in the time required for thermal equilibration at each temperature. The chosen procedure was therefore that the temperature was kept constant and chloride added in approximately 5 mol anion % increments as (Na,K)Cl pellets. At the end of each experiment, the chloride content of a solidified melt sample was obtained by titration with mercury(II) nitrate (22), a method not susceptible to interference by sulfate. In all cases the chloride content was within ± 2 mol anion % of the expected value.

Chloride additions to the (Na,K,Al)SO₄ melt encouraged gradual decomposition of the melt, evidenced by the formation of a precipitate, shown to be Al₂O₃ upon microanalysis. Thus at the highest temperature (730°C), chloride additions were limited to 45 mol anion % for nickel, since a larger wavelength scan range was required for this ion, and thus each spectrum took longer to record.
NICKEL(II)

Results

The variation of the nickel(II) spectrum with chloride content from 0 to 35 mol anion % was recorded over the temperature range 587-720°C, although at 587°C the system was very near its melting point and too opaque for recordings at chloride content below 15 mol anion %. The variation with chloride content at 600°C is shown in Figure 2 and at 720°C in Figure 3.

The spectrum of nickel(II) in the (Na,K,Al)SO₄ melt (i.e. no chloride) is similar to that in the (Li,Na,K)SO₄ melt (5), except that the shoulder on the low energy side of the main band is much more pronounced in the aluminum-containing melt. The effect of increasing temperature is to shift the whole spectrum to slightly lower energy and introduce a second shoulder on the low energy side of the main band. The progressive broadening of bands with increasing temperature tended to mask these effects.

The addition of chloride ions has a dramatic effect on the spectra at all temperatures. As the chloride content is increased, the original main band diminishes and the spectra become dominated by bands emerging at lower energies. The addition of chloride is also accompanied by the establishment of a number of isosbestic points at approximately 10,000, 12,000, 20,000 and 25,000 cm⁻¹. However, not all the curves pass through these points and there is an apparent improvement in the convergence with increasing temperature. The relatively poor definition of the 25,000 cm⁻¹ isosbestic point results, in part, especially at the higher temperatures, from the onset of precipitation of alumina (spectra were recorded from high to low wavelengths). The appearance of isosbestic points has generally been taken as evidence for the presence of a two-species equilibrium. However, this is not always so, and a more rigorous analysis, based on internal linearity theory, must be performed. We therefore report at this time that with chloride concentrations greater than around 20 mol anion % we have found, and will describe elsewhere, that two species predominate in solution, NiCl₄²⁻ (with probably a distorted rather than regular tetrahedral geometry) and NiCl₃(SO₄)ₓ²⁻ (an octahedral complex, in which the number of sulfate ligands is uncertain, since these ligands could be either mono or bidentate, but we favor x = 2, with two bidentate sulfates).

To establish the effect of complete replacement of sulfate by chloride in the melt, the spectrum of nickel(II)
chloride in the (Na,K,Al)Cl melt, having the same cation ratios as the (Na,K,Al)SO₄ system, was recorded at 692°C. This is shown in Figure 4, along with the spectra for chloride additions to the sulfate melt at that temperature. The spectrum in (Na,K,Al)Cl is very similar to that for nickel(II) in fused CsCl at 800°C, reported by Smith (23).

Higher Derivative Analysis

Both second and fourth derivative analyses were performed, and good agreement between the two found. Simultaneous smoothing and differentiation was utilized, equivalent to a 49 point differentiation of a 49 point smooth spectrum, fitting a fifth order polynomial. The uncertainty in the energies of the band positions obtained was estimated as 200 cm⁻¹.

For the spectra in the (Na,K,Al)(SO₄,Cl) system, up to six bands were identified. Representative second and fourth derivatives are shown in Figure 5. The variation of the energies of the resolved bands with chloride content was investigated at six temperatures, examples being given in Figure 6.

Discussion

In the spectrochemical series for molten salts, reported by Johnson (24), sulfate appears directly above chloride. We should therefore expect a slight shift to lower energies if sulfate ligands were replaced by chloride in the nickel coordination sphere. The interpretation of the mixed sulfate-chloride spectra is aided by the results from the analysis of nickel(II) in (Na,K,Al)Cl, and so this is considered first.

The similarity of the nickel(II) spectra in fused CsCl and in a crystal of Cs₂ZnCl₄ doped with Cs₂NiCl₄, in which nickel ions are known to be tetrahedrally coordinated, led Smith (23) to conclude that nickel complexes of T₄ symmetry were present in the CsCl melt. The same conclusion may be drawn here, regarding nickel(II) in the (Na,K,Al)Cl melt. Assuming a Dq value of 370 cm⁻¹ for the NiCl₂⁻ complex (23), the bands at 14,300, 15,800 and 17,500 cm⁻¹ may be assigned to the 3T₁(F) → 3T₁(F) transition. Three distinct bands have been observed as a result of splitting of the triplet states by spin-orbit coupling (23). The band at 13,400 cm⁻¹, which is much less pronounced than the rest, may be assigned to the spin-forbidden transition 3T₁(F) → 1E(D) or 1T₂(D).

Of the six transitions identified in the spectra of the mixed sulfate-chloride melts, four may be associated...
with the above bands found in the \((\text{Na,K,Al})\text{Cl}\) melt. The remaining two, around 22,000 and 24,000 \(\text{cm}^{-1}\), depending upon the temperature and mol anion \% chloride, may be assigned to transitions of an octahedral complex. The main band, at 22,000 \(\text{cm}^{-1}\), corresponds to the \(3A_2g \rightarrow 3T_1g (P)\) transition, while the weak band may be assigned to \(d^3\) spin-forbidden transition to the \(^1A_1g\) or \(^1T_1g\) state, from the \(^1G\) free ion term.

Thus, in the mixed sulfate-chloride melts we have both octahedral and tetrahedral nickel(II) species. The octahedral complex clearly commences as \(\text{Ni(SO}_4\text{)}^{4-}\) (strictly, it has \(D_3\) symmetry, but the crystal field of the metal ion may be taken as \(O_h\)), with three bidentate sulfate ligands. This has been observed in sulfate melts by other workers (5). The steady shift to lower energies as chloride concentration is increased implies that chloride is progressively being substituted for sulfate. The most likely course is for one sulfate ligand to become monodentate as one chloride ligand enters, and then this sulfate is replaced by a second chloride, forming a \textit{cis}-dichlorosulfato nickel(II) complex.

The tetrahedral species are more rapidly converted to \(\text{NiCl}_4^{2-}\) as shown by the positions of the four bands tending to constant energies above around 20 mol anion \% chloride. Below this concentration various tetrahedral chlorosulfato complexes are present, but because of the greater distance to be spanned by a bidentate sulfato ligand in a tetrahedral complex, compared with an octahedral complex, we anticipate that here all sulfato ligands are monodentate.

In the case of nickel(II) in pure sulfate melts the ligand field spectra have previously been interpreted in terms of only an octahedral nickel complex present, \(\text{Ni(SO}_4\text{)}^{4-}\) (5). The spectrum of nickel(II) in \((\text{Li,Na,K})\text{SO}_4\) at 640°C (Figure 7) compares well with the featureless spectrum reported at 550°C by Johnson and Piper (5). The composite non-Gaussian nature of the principle visible band has been pointed out (23) and the possibility of distortion from pure octahedrality raised. A reinvestigation of this spectrum (25), including a test of Beer's law in the range 5-25 \(\times 10^{-5}\) M, confirmed most of the original features but showed a more pronounced shoulder on the low energy side of the main band, and a slight saddle at the maximum of the band at 10,000 \(\text{cm}^{-1}\). The resolution of the spectrum into Gaussian components gave neither a unique nor a decipherable result, but additional bands at 18,000 and 19,500 \(\text{cm}^{-1}\) were reported. These are more clearly seen in our aluminum-containing sulfate melt (Figure 7).
Examination of our second and fourth differential spectra of nickel(II) in (Na,K,Al)SO₄ all showed two bands in this region: at 600°C they were at 18,100 and 19,600 cm⁻¹. This is consistent with the mixed chloro-sulfato melts, where the data extrapolated back to bands in this region in the absence of chloride. Thus we can explain the observed asymmetry: sulfate melts containing nickel(II) have both octahedral and tetrahedral sulfato complexes. The latter is attributed to Ni(SO₄)₄⁶⁻, all the sulfate ligands being monodentate.

CHROMIUM(III)

Results

The effect of chlorides on the spectrum of Cr(III) in (Na,K,Al)SO₄ is comparatively small and virtually temperature independent in the range examined (610-730°C). An example is given in Figure 8, which also includes the spectrum of Cr(III) in the (Na,K,Al)Cl melt.

The effect of increasing temperature upon the spectrum in the pure sulfate melt is to produce a slight shift to lower energy. Additionally the doublet at approximately 14,000 cm⁻¹ becomes less pronounced, due to thermal broadening.

Chloride additions also cause a shift to lower energy, but of greater magnitude than that due to increasing temperature. The effect on the smaller band of the spectrum is interesting in that chloride addition appears to increase the intensity of the lower energy component of the doublet which comprises this band.

In the (Na,K,Al)SO₄ melt, the Cr(III) spectrum is at lower energy than when recorded in the mixed sulfate-chloride system, with sharper, more intense bands. After a few hours, and especially at the higher temperatures, chromium(III) ions begin to decompose, in both (Na,K,Al)SO₄ and in the presence of chloride. The absorption edge around 24,000 cm⁻¹ increases, and the d—d bands decrease. A green precipitate is formed in the melt, identified as Cr₂O₃ by elemental analysis. If synthetic flue gas, containing both SO₂ and SO₃, is passed over the melt the rate of decomposition is reduced.

Higher Derivative Analysis

The analysis chosen as best for the chromium spectra was equivalent to a 47 point differentiation of a 47 point smoothed spectrum, with a fifth order polynomial. A
typical result is shown in Figure 9. The bands obtained were closely spaced and therefore not always resolved by the second derivative. However, in cases where resolution was possible, good agreement between second and fourth derivatives was obtained. When a band was not clearly resolved in the second derivative, the value obtained from the fourth derivative alone was used. Small separations of the component bands sometimes led to failure to locate all bands present.

Up to ten bands, initially designated A–J, were obtained, and examples of the variation of their energies with chloride content is shown in Figure 10, together with their assignments. For the spectrum in the (Na,K,Al)Cl melt, the corresponding energies of the corresponding bands are, in descending order: A, 18,400; B, 17,600; C, 16,700; D, not observed; E, 16,000; F, 15,200; G, 14,400; H, 13,600; I, 12,800; and J, 11,700 cm⁻¹.

Discussion

The chromium(II) ion is highly stabilized in octahedral site symmetry, and we may therefore conclude that the species Cr(SO₄)₂⁻ is present in the (Na,K,Al)SO₄ melt. The two main bands in the spectra may therefore be assigned to the transitions ⁴A₂ → ⁴T₂g(F) and ⁴A₂ → ⁴T₁g(F). A third band, at higher energy, due to the transition ³A₂ → ³T¹(F), is in this case masked by the charge transfer absorption edge. The values for Δ(10Dq), the crystal field splitting parameter, for octahedral Cr(SO₄)₂⁻ and for CrCl₆⁻ are similar, 12,000 and 14,300 cm⁻¹ respectively, and thus using the Tanabe and Sugano diagram for ³A₂ octahedral species the spin-forbidden transitions, ⁴A₂ → ⁵T¹(G) and ⁵E(G), are expected between the two main bands. Differentiation is therefore expected to resolve both main bands into the three components of their triplets, and the spin-forbidden bands into three and two components, respectively. The spin-forbidden triplet is likely to resolve into a doublet and a singlet, the separation in the doublet possibly being small. Since both spin-forbidden transitions are not well separated according to the Sugano and Tanabe diagram assignment of some of the bands identified by differentiation is not unambiguous.

However, we can assign bands A–C to the ⁴A₂ → ⁴T₁g(F) transition, and by careful comparison of the recorded and the differentiated spectra we can, with reasonable confidence, assign bands H–J to the ⁴A₂ → ⁴T₂g(F) transition. This leaves the four intervening bands D–G. Since the ⁵E(G) transition is expected at lower energy than the ⁵T¹(G) band G is assigned to the lower energy component
of the $^2\text{E}(\text{G})$ doublet. We suggest that the other component of this transition is band $\text{F}$, and that bands $\text{D}$ and $\text{E}$ are, respectively, the singlet and unresolved doublet of the $^2\text{T}_1(\text{G})$ transition.

It may be observed in Figure 8 that the two main bands in the sulfate melt are broader than in the chloride melt. This is the result of distortion from octahedral symmetry. Whole both $\text{CrCl}_6^{3-}$ and $\text{Cr(SO}_4\text{)}_3^{3-}$ are both octahedral complexes the former has $O_h$ symmetry and the latter $D_3$ symmetry. This results in splitting the $O_h$ levels as follows (26):

$$A_{2g}(O_h) \rightarrow A_2(D_3) \text{ i.e. unchanged},$$
$$T_{2g}(O_h) \rightarrow E(D_3) + A_1(D_3),$$
$$\text{and } T_{1g}(O_h) \rightarrow E(D_3) + A_2(D_3).$$

These splittings are greater in magnitude than those due to spin-orbit coupling, discussed above, and thus result in the observed broadening of the sulfate main bands, and also in the appearance of the doublet just discernible in the lower energy band in Figure 8: this doublet is better resolved at lower temperatures.

The effect of chloride additions on the spectrum is far less dramatic than in the case of nickel. This is to be expected, since for the chromium(III) ion no change in coordination occurs and, as already mentioned, chloride is directly below sulfate in the spectrochemical series for molten salts (24). Figure 8 also shows that the spectrum for the melt containing 45 mol anion % chloride, the maximum employed, is not shifted even half-way towards that for the $\text{CrCl}_6^{3-}$ ion in the (Na,K,Al)Cl melt. Thus although we obviously now have a mixed chloride-sulfate coordination sphere around the chromium(III) ion, the bidentate sulfate is here clearly the more strongly held and a less readily displaced ligand, unlike in the nickel situation.

A measure of the ratio of chloride-to-sulfate ligands may be obtained from the values of the crystal field splitting parameter, $\Delta_0$, the energy of the $^4\text{A}_2 \rightarrow ^4\text{T}_{2g}(\text{F})$ transition, reported above. (The value of 14,300 cm$^{-1}$ for $\text{Cr(SO}_4\text{)}_3^{3-}$ was taken as the center of the doublet.) It is clearly difficult to locate the center of this transition for the 45 mol anion % chloride spectrum, and strictly its energy is no longer precisely equal to $\Delta_0$ (see below), but a value of 13,500 cm$^{-1}$ may be taken as a reasonable approximation. This gives an oxygen-to-chlorine ratio of 4:2 in the coordination sphere,
corresponding to Cr(SO$_4$)$_2$Cl$_2$$^-$, with two bidentate sulfates. Although the complex could be Cr(SO$_4$)$_2$Cl$_2$$^-$, with two mono and one bidentate sulfate ligands, this is unlikely on charge and steric considerations. Thus Cr(SO$_4$)$_2$Cl$_2$$^-$ is a cis-complex, it being improbable that in the formation of this complex one or both of the two remaining sulfates would rearrange one of their coordination sites. Further evidence to support a cis-complex is now given.

An examination of the addition of chloride upon the energies of the resolved bands (Figure 10) shows that bands A–C, the components of the $4A_2 \rightarrow 4T_1g(F)$ transition decrease in energy, but the components of the $4A_2 \rightarrow 4T_2g(F)$, bands H–J, decrease only slightly. Bands D–E are essentially independent of chloride concentration, as the spin-forbidden transitions to $2T_2^1(G)$ and $2E(G)$ are field-independent, and thus no shift is here expected on reducing $\Delta_0$. Now since the $4T_1g(F)$ band is shifted more than the $4T_2g(F)$ band, this must be explained in terms of symmetry changes on going from a [CrA$_r$] complex to one represented by [CrA$_r$B$_2$] (26). Here A and B represent the ligand atoms occupying the six coordination sites, and here A represents oxygen and B, chlorine, in a cis-complex. Such a complex has C$_{2v}$ symmetry, and this results in the splitting of the original $T_2g(F)$ and $T_1g(F)$ terms into components, viz.,

$$T_1g \rightarrow B_2^1, A_2^1, A_1^1,$$

and

$$T_2g \rightarrow B_2^2, A_2^2, A_1^2.$$

Both pairs of levels are at lower energies than the terms from which they arose, but the shifts for the $B_2^1, A_2^1$ and $B_1^1, A_2^1$ levels of the $T_1g$ term are greater than those for the $B_2^2, A_2^2$ and $A_2^2$ levels from the $T_2g$ term. Thus, the change in configuration has a greater effect (superimposed upon the overall shift resulting from a reduction in $\Delta_0$) on the levels originating from $T_1g$ than those from $T_2g$. The net result is that, as observed, the higher energy band is shifted to a greater degree than the lower energy peak.

IRON(III)

Results

The spectrum of iron(III) in the (Na,K,Al)SO$_4$ melt is dominated by a strong ligand-to-metal charge transfer edge, which completely swamps the weak, spin-forbidden $d-d$ transitions. The effect of chloride addition is to shift this edge progressively to lower energy (Figure 11).
Increasing the temperature has the same effect. Additionally, weak bands begin to appear on the rising edge, (Figure 12), though they are never of sufficient intensity to form a well-defined shoulder. The spectrum of iron(III) in the (Na,K,Al)Cl melt is also shown in this Figure. With the complete replacement of sulfate by chloride the edge is shifted further into the visible region. The weak bands evident at lower chloride contents are no longer apparent.

No decomposition of the iron(III) species was observed during the few hours lifetime of these experiments. Neither was decomposition of iron(III) observed in molten (Na,K,Al)SO₄, held at 805°C for six hours. However, as discussed in our previous contribution, deposition of Fe₂O₃ is believed to be slow.

Higher Derivative Analysis

Second and fourth derivative analyses were performed, and the optimum derivatives were obtained using a 35 point derivative of a 35 point smoothed spectrum, with a polynomial of order five. A large number of weak, closely spaced bonds were identified. First impressions might be that these bands could be noise and thus spurious, but their number, and peak positions are self-consistent among all the iron(III) spectra recorded. The bands can be identified in sets of spectra and at different temperatures: spurious noise bands would be randomly distributed. Further, their derivative intensities are comparable with, but slightly less than, those of the bands found in the spectra of nickel(II) and chromium(III), and, as we shall show, satisfactory crystal field assignments can be made for these observed bands.

The variation of the band energies with chloride content was small, and temperature independent. A representative plot is shown in Figure 13. Typical second and fourth derivative spectra are shown in Figure 14. Initially we label the bands alphabetically, in order of decreasing energy. Since temperature and chloride content increase shifts the charge transfer band edge to lower energies, bands A-C cannot always be located. In the pure chloride melt, (Na,K,Al)Cl, the following bands were identified (energies in cm⁻¹): D, 18,800; E, 18,300; F, 17,700; H, 16,900; I, 15,900; K, 15,100; and M, 13,200. Bands corresponding in the mixed sulfato-chloro melts to G, J and L were not located, and as expected, the bands A-C were beyond the absorbance range of the spectrophotometer and could therefore not be detected.
Discussion

Since all the $d-d$ transitions for a $d^5$ ion are spin-forbidden, their intensities are generally too low for bands to be detected unless enhanced by derivative analysis.

The pattern of crystal field splitting for a $d^5$ ion is the same in both octahedral and tetrahedral fields. Thus the only changes expected as a consequence of coordination change would be those resulting from a variation in $\Delta$, since $\Delta(\text{tet}) = -4/9\Delta(\text{oct})$. Since chloride and sulfate have adjacent positions in the spectrochemical series for molten salts (24) and the energies of the resolved bands are virtually independent of chloride concentration it is concluded that no coordination change takes place with increase in chloride content.

For a $d^5$ ion there is no net change in crystal field stabilization energy on going from octahedral to tetrahedral coordination. Electrostatic factors will favor four-fold coordination. We may therefore assumed that FeCl$_4^-$ ions are present in (Na,K,Al)Cl. And consequently, in the pure sulfate melt a tetrahedral complex of iron(III) will be present, viz., Fe(SO$_4$)$_4^{5-}$. We again anticipate that a bidentate sulfate cannot span the distance between two adjacent tetrahedral sites.

The degree of sulfate replacement by chloride as chloride concentration is increased is difficult to gauge. The shift of the absorption edge to lower energy on the addition of chloride indicates chloride participation in the ligand-to-metal charge transfer process, since its lower electronegativity reduces the energy of the transition. However, the absorbance of the charge transfer band at some fixed wavelength is not generally as sensitive an indicator of coordination sphere composition as the crystal field splitting, which in this case shows no discernible trends.

The observed bands may be assigned with reference to the spectrum of FeCl$_4^-$ in acetone at room temperature (27), and in the solid pyridinium salt (PyH)$_2$Fe$_2$Cl$_9$ at 20 K (28). The bands reported were identified by eye.

The assignments for the FeCl$_4^-$ spectrum are complex. Balt (27) has discussed possible assignments of the bands, taking account of the pronounced nephelauxetic effect known to exist in this ion. The bands in the spectrum of iron(III) in our sulfate and chloride melts have been identified on the basis of these assignments. The results are presented in Table 1.
Table 1. Comparison of Maxima (cm\(^{-1}\)) of Resolved Bands from Iron(III) Spectrum in (Na,K,Al)SO\(_4\) and (Na,K,Al)Cl Melts with the Reported Maxima of FeCl\(_4^-\).

| Band | Assignment | FeCl\(_4^-\) in acetone at 300 K | FeCl\(_4^-\) in (PyH\(_2\))Fe\(_2\)Cl\(_9\) at 20 K | Fe(III) in (Na,K,Al)Cl at 972 K | Fe(III) in (Na,K,Al)SO\(_4\) at 1003 K |
|------|------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| A    | \(4T_1(4P)\) | 22,000\(^a\)                    | 22,100                          | nf\(^b\)                       | 21,500                          |
| B    |            | nf                              | nf                             | nf                             | 20,900                          |
| C    |            | nf                              | nf                             | nf                             | 20,000                          |
| D    | \(2\Gamma\) | nf                              | 19,750                         | nf                             | 19,500                          |
| E    | \(4E(4D)\) | 18,760                          | 18,800                         | 18,800                         | 18,700                          |
| F    |            | nf                              | nf                             | 18,300                         | 18,300                          |
| G    | \(2\Gamma\) | nf                              | 17,800                         | 17,700                         | 17,600                          |
| H    | \(4T_2(4D)\) | 16,700                          | 16,500                         | 16,900                         | 16,700                          |
| I    | \(4A_1(4G)\) | 16,150                          | 16,150                         | 15,900                         | 16,200                          |
| J    | \(4E(4G)\) | nf                              | 15,650                         | nf                             | 15,600\(^c\)                   |
| K    |            | nf                              | 15,100                         | nf                             | 15,100                          |
| L    | \(4T_2(4G)\) | 14,600                          | 14,600                         | nf                             | 14,400                          |
| M    | \(4T_1(4G)\) | 13,700                          | 13,700                         | 13,200                         | 13,400                          |

\(^a\), 883 K; \(^b\), nf = not found; \(^c\), 943 K.
Assignments designated $^2I$ by Balt represent transitions to unspecified doublet terms, arising from the $^2I$ free ion state. These were observed in the solid state FeCl$_4^-$ spectrum but not in solution. Bands B, C, F and K observed in this work have not been detected in the acetone or solid state spectra of FeCl$_4^-$. They may be assigned to further sextet-doublet transitions, or possibly splitting of the quartet term states. It is to be expected that more bands would be identified in this study than were found previously since, as already mentioned, previous identifications relied solely on examination by eye of the recorded spectrum. Band A was not found in the pure chloride melt because it was out of the absorbance range of the spectrophotometer. The value reported for A in the sulfate melt was obtained in low temperature melts only.

It is also to be expected that the FeCl$_4^-$ spectrum observed at 20$^\circ$K would reveal more bands than the number seen at ambient temperatures. We would point out that from our spectra, recorded nearly 1000$^\circ$C higher, were found these low temperature bands, and more. We also note that most of the band maxima identified for FeCl$_4^-$ in molten (Na,K,Al)SO$_4$, generally within experimental error the same as those reported at 20 K, were also generally at slightly lower energy, shifted in the direction expected with temperature increase.

Comparison of the peak maxima identified in the sulfate and chloride melts reveals that, for tetrahedral complexes of iron(III), sulfate and chloride have identical, rather than adjacent (24), positions in the spectrochemical series for molten salts, in contrast to our chromium results.

Thus in the case of iron(III), differentiation of observed spectra has been shown to be a powerful and sufficiently precise technique for identifying spin-forbidden bands, even when broadened by high temperatures. Differentiation of the spectrum of FeCl$_4^-$ at 20 K should therefore reveal the additional bands we now report, plus possibly some more, such that the at present unassigned bands can be identified with sextet-doublet transitions, or splittings of quartet term states, or vibronic transitions.

CONCLUSION

We have shown that various chloro-sulfato complexes of the transition elements nickel, chromium and iron are formed when chloride is added to (Na,K,Al)SO$_4$ melts containing these metals. The implication for power
generation plant turning to high-chlorine coals is that, where chlorine-containing complex ions are readily formed at low chloride concentrations (the chlorine content of, say, superheater tube salt deposits is not expected to exceed a few mole %) then corrosion will be increased. This will apply to the corrosion of nickel and iron, but not to chromium, where sulfate ligands are not readily replaced by chloride. The basic reason for accelerated corrosion is that these complexes are smaller than sulfato complexes and will thus diffuse faster across the thermal gradient.

It must be stressed that confirmation is awaited, and is expected from our present determinations of corrosion rates for these three elements as a function of chloride concentration. We would caution that determinations of corrosion rates for various stainless steels in molten (Na,K,Al)SO₄, and with added chloride using our technique, described in our earlier paper, are also required before any quantitative predictions of corrosion rates can be attempted.

We can however say that the development of our new technique has shown such determinations a ready reality, and our computer treatment of spectra has revealed a considerable body of information concerning the nature, properties and geometries of the corrosion products that will be formed.

ACKNOWLEDGMENTS

We thank Dr. P. Gans for valued discussions. K.K. acknowledges a CASE Research Studentship with the Science Research Council and the Central Electricity Generating Board, Harrogate, West Yorkshire.

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Figure 1. First four derivatives of a simulated Gaussian absorption profile (ordinate scales not comparable).

Figure 2. Variation of nickel(II) spectrum in (Na,K,Al)(SO₄,Cl) with chloride content at 600°C (49 point smoothing; fifth order polynomial).
Figure 3. As for Figure 2, at 720°C.

Figure 4. As for Figure 2, at 692°C. Dashed line, (Na,K,Al)Cl melt.
Figure 5. Spectrum of nickel(II) in (Na,K,Al)(SO₄,Cl), containing 10 mol anion % chloride at 692°C and its second and fourth derivative.

Figure 6. Variation and assignments of resolved bands of nickel(II) in (Na,K,Al)(SO₄,Cl).
Figure 7. Comparison of nickel(II) spectra at 640°C.

Figure 8. Effect of chloride addition on chromium(III) spectrum in (Na,K,Al)SO₄ at 595°C (47 point smoothing, fifth order polynomial.)
Figure 9. Spectrum of chromium(III) in (Na,K,Al)(SO₄,Cl) containing 20 mol anion % chloride at 640°C and its second and fourth derivative.

Figure 10. Variation and assignments of resolved bands of chromium(III) in (Na,K,Al)(SO₄,Cl).
Figure 11. Effect of chloride addition on iron(III) spectrum in (Na,K,Al)$_2$S$_2$O$_4$ at 610°C (35 point smoothing, fifth order polynomial).

Figure 12. As for Figure 11 at 699°C (47 point smoothing, fifth order polynomial). Dashed line, (Na,K,Al)Cl melt.
Figure 13. Variation of resolved bands of iron(III) in (Na,K,Al)(SO₄,Cl) at 610°C.

Figure 14. Spectrum of iron(III) in (Na,K,Al)(SO₄,Cl) containing 20 mol anion % chloride at 640°C and its second and fourth derivative.