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The Application of Ionic Nanoparticles in the Conservation of Archaelogical Wood

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Summary: A potential method for the de-acidification of water-logged archaeological wood is through a treatment with alkaline nanoparticles. In previous studies, we have shown that strontium carbonate nanoparticles are especially effective in removing sulfuric acid from the *Mary Rose* timbers. In this contribution, we report the effect of these nanoparticles on other known sulfur compounds in the timbers. Overall, these effects are beneficial, yielding benign compounds and removing the possibility for the conversion to sulfuric acid.

Keywords: cysteine; cystine; *Mary Rose*; methionine; nanoparticles; natrojarosite; pyrite; strontium carbonate; sulfur problem

Introduction

A major cause of the degradation of heritage and museum objects is attack by acid. Examples include the attack caused by atmospheric pollution (see, for example reference[1]) or acidic species generated from within the artefact. In the case of cellulose based materials, paper and wood, acid causes hydrolysis of the polymer and a loss of mechanical strength. Manuscripts written with iron-gall ink, from the 12th to the 20th centuries the most common writing ink, have posed a particular conservation problem.[2] The colour forming ingredients are the product of a reaction between gallic acid, from tannins, and iron ions from iron (II) sulfate, which meant that the ink was often contaminated with acid. Similar problems have been encountered in water-logged wooden ships, such as the *Vasa* and the *Mary Rose*, where the timbers are being degraded by sulfuric acid and reactions catalysed by iron.[3–8] Amongst marine archaeologists, this is often referred to as 'the sulfur problem'.

We are particularly concerned with the degradation of the timbers of the *Mary Rose*. It sank on July 1545 whilst en route to confront ships of the French fleet outside Portsmouth harbour. It remained on the seabed for over 400 years before it was uncovered and then raised in 1982. Approximately half of the ship survived as a consequence of being buried by silt, and thereby protected from the currents and from the organisms that eroded away the exposed timbers. However, the surviving timbers now exhibit potentially damaging sulfur salt precipitates. The problem was first identified in 2000 in the conserved Swedish warship, *Vasa*.[3–5] The origin of the precipitates is the formation of H_2S in the polluted sea of the harbour by sulfur reducing bacteria that diffuses into the wood and reacts to form a range of reduced sulfur compounds. In the anoxic conditions of the seabed, these materials are not a problem but in the raised timbers, air causes oxidation, the formation of sulfuric acid with degradation of the cellulose and formation of the mineral deposits. The growth of these deposits causes further disruption of the timber as the growing crystals crack the wood. The problems are

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further exacerbated by the presence of iron species in the wood (from original fittings, bolts and nails) which catalyse the formation of sulfuric acid. It has been estimated that the Mary Rose timbers contain some 2 tonnes of sulfur compounds[5] which X-ray absorption near edge spectroscopy (XANES) has shown to be in the form of elemental sulfur, various organosulfur compounds (e.g. thiols, cysteine, cystine, etc.) and iron sulfides.[4–6] The removal of these compounds in many cases is not feasible as many of the potential solvents would cause damage to the wood. However, although the removal of iron is possible with various chelating agents,[4,8] the oxidation of the reduced sulfur compounds is a long-term threat to the timbers. We have been exploring the use of alkaline nanoparticles impregnated into the timbers to act as a reservoir to neutralise acid in the wood.[7] This approach was pioneered by Baglioni and co-workers[9–15] who used nanoparticles of alkaline earth hydroxides to de-acidify a range of heritage artefacts and proposed their application as a treatment of the sulfur problem in the Vasa and other water-logged shipwrecks.[13–15] In their experiments on timbers these workers used dispersions of nanoparticles of $Ca(OH)_2$ and $Mg(OH)_2$, with particle sizes of ~100 nm, in 2-propanol to permeate into the wood. These were very successful in de-acidifying the wood and had the advantage over other methods as the nanoparticles being smaller than the wood lumen could readily diffuse into the artefacts. We have used modifications of the alkaline nanoparticle approach for de-acidifications.[7] Firstly, we have used alkaline earth carbonates as these are readily produced as nanoparticles by high-energy ball milling and particle sizes of 20–50 nm can be readily achieved. Secondly, we have focused on the use of $SrCO_3$ as our main characterisation techniques have used the X-ray fluorescence signal of the strontium. Water-logged timbers contain varying degrees of calcium and magnesium and these would interfere with our measurements if we used these ions in the de-acidification treatment, i.e. there would be a non-zero background to the measurements. We have shown that dispersions of nanoparticles of $SrCO_3$ in 2-propanol will not only de-acidify samples of Mary Rose timbers but will also react and stabilise other reduced sulfur compounds in the wood.[7] In addition we have measured the diffusion rate of the nanoparticles into wood.[16] This observation is briefly outlined below.

The evidence for the effectiveness of the $SrCO_3$ nanoparticles in treating the *Mary Rose* timbers is seen in the S K-edge XANES data[7] and a typical result is shown in Figure 1. The timber was treated with a dispersion of nanoparticles in 2-propanol for three days. The key features of the figure are that after treatment, the peak due to reduced sulfur species (~2473 eV) is decreased and the peak due to sulfate (~2483 eV) is increased. The three dashed vertical lines mark features due to strontium sulfate, $SrSO_4$. As the peak sizes are proportional to concentration, the plot indicates that there are reactions of the nanoparticles with reduced sulfur compounds. The aim of this contribution is to obtain a better understanding of the possible reactions by probing in the laboratory the reaction of $SrCO_3$ nanoparticles with individual sulfur species

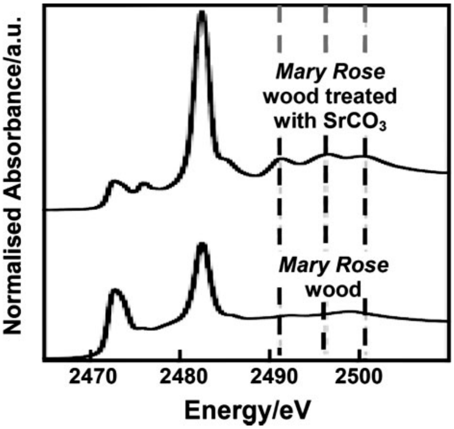

Figure 1.
Sulfur K-edge XANES spectra for *Mary Rose* timber before and after treatment with $SrCO_3$ nanoparticles. For details see text.

known to be present in the *Mary Rose* timbers. In the timbers, the presence of moisture will be essential, as reactions with $SrCO_3$ will involve ionic species. Hence, we have conducted the reactions in water to accelerate any possible processes. We have also included a study of the reaction with natrojarosite, $NaFe_3(SO_4)_2(OH)_6$, an oxidised sulfur compound which is common in the timbers and has a very low water solubility.

Experimental Part

Materials

Flowers of sulfur and amino acids (L-cysteine, L-cystine and L-methionine) were purchased from Sigma-Aldrich. Pyrite, FeS_2, was purchased from Fisher Chemicals Ltd. Natrojarosite was prepared using literature procedures.[17] Nanoparticle $SrCO_3$ were prepared by ball milling powder (Sigma–Aldrich, ≥99.9% pure on a trace metals basis) using an alumina ceramic vial and balls for 8 h using a SPEX 8000 M Mixer/Mill. The particle size, based on a Scherrer analysis of the XRD peak widths was 20-50 nm.[16]

Procedure

Equimolar mixtures of the target compound and nanoparticle $SrCO_3$ were made to give a total mass of 5 g. The mixtures were placed in plastic vials, 10 ml of distilled water were added and the vials sonicated for 28 days at 20°C. The mixtures were then allowed to evaporate to dryness in an oven at 60°C.

Characterisation

X-ray powder diffraction patterns of mixtures containing inorganic target compounds were collected on a Philips PW1720 conventional laboratory diffractometer using a Cu Kα tube operating at 35 kV and 20 mA.

Electro spray mass spectra were recorded on a Bruker micrOTOF-Q II mass spectrometer. Samples were separated on-line by reverse-phase HPLC on a Phenomenex Synergi Hydro-RP column (C18, 2.5 μm, 100Å, 2.0 mm x 50 mm) running on an Agilent 1100 HPLC system at a flow rate of 0.2 ml/min using a water, acetonitrile, 0.05% trifluoroacetic acid gradient. The eluant was monitored at 214 nm and then directed into the electro spray source, operating in positive ion mode, at 4.5 kV and mass spectra recorded from 50-3000 m/z. Data was analysed with Bruker's Compass Data Analysis software.

Results and Discussion

The simplest way to present the results is to treat each compound that we have investigated individually.

Natrojarosite

The reaction between iron sulfates (Fe(II) and Fe(III)) and nanoparticle $SrCO_3$ is fast and leads to the formations of $SrSO_4$ and siderite (iron carbonate, $FeCO_3$).[16] The reaction rate of the nanoparticles with natrojarosite had not been monitored. A mixture of natrojarosite and the nanoparticles in water was sonicated for 7 days, the mixture dried and an XRD pattern collected. This pattern is shown in Figure 2. The dominant peaks in the pattern are due to natrojarosite and $SrCO_3$, however there are peaks that are unambiguously from $SrSO_4$ and these are marked in the figure. Thus there is a reaction between natrojarosite and $SrCO_3$, as with the iron sulfates, albeit at a much slower rate.

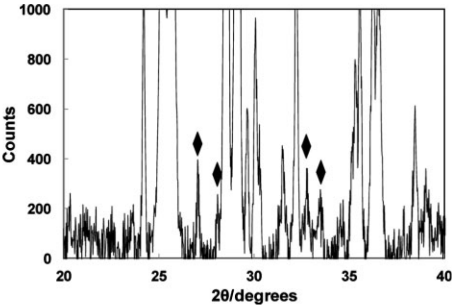

Figure 2.
The XRD pattern of Natrojarosite and nanoparticle $SrCO_3$ after 7 days reaction. The diamonds mark peaks due to $SrSO_4$.

Elemental Sulfur

The mixture of sulfur and nanoparticle $SrCO_3$ was sonicated for 28 days. At the end of this period the XRD pattern revealed only peaks due to the starting components. Hence, if there is any reaction it is extremely slow.

Pyrite

The mixture of pyrite and nanoparticle $SrCO_3$ was sonicated for 28 days, dried and the XRD pattern collected. The pattern, shown in Figure 3 shows three additional peaks which index as siderite, $FeCO_3$. This clearly indicates a reaction between the components.

There have been extensive studies [18–24] of the rate and mechanism of pyrite oxidation due to its importance in the mining industry (in mineral processing, metal extraction, and acid mine drainage). The situation is complex and the process is dependent on temperature and pH. Pyrite has a negligible solubility in water and in most cases the oxidation is assumed to take place at the crystal surface as a result of the reaction with molecular oxygen. In general, the oxidation rate is increased with increasing temperature, pH and reagent concentration. The reaction between pyrite and aqueous sodium carbonate was studied by Descostes *et al* [21] and Ciminelli and co-workers [22–24] and the latter is the study that is most comparable to the present experiments. These workers found that after 24 hours, pyrite in 0.1 mol sodium carbonate/bicarbonate solution at 80°C yielded peaks in the XRD pattern due to ferrihydrite ($Fe_5HO_8.4H_2O$), siderite, and iron carbonate hydroxide ($Fe_2(OH)_2CO_3$). Thus, the results are very similar to the findings in the present work.

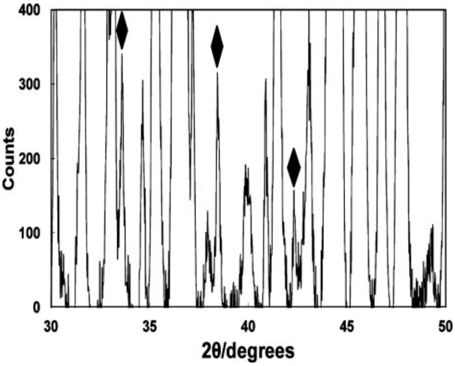

Figure 3.
The XRD pattern of pyrite and nanoparticle $SrCO_3$ after 28 days reaction. The diamonds mark peaks due to siderite, $FeCO_3$.

This observation of a direct reaction between nanoparticle strontium carbonate and pyrite is an important finding in terms of explaining the S XANES work in the *Mary Rose*[7] that was summarised in the Introduction; namely, treatment with nanoparticle strontium carbonate lowers the concentration of reduced sulfur species. We now have direct proof that nanoparticle strontium carbonate will oxidise pyrite. Under the current conditions, the reaction was slow; however, in the treatment of the *Mary Rose* timbers, the strontium carbonate concentration exceeded that of pyrite and reaction should be fast.

Amino Acids

The mass spectra of the aqueous mixtures of the amino acids and nanoparticle $SrCO_3$ were collected after 28 days. In all three systems, the spectra contained peaks at mass/charge ratios (m/z) and in concentrations considerably larger than that expected for the parent amino acid. In addition, the fine detail around a dominant peak exhibited a spread consistent with the isotopic abundances of strontium. Hence, a reaction had occurred between $SrCO_3$ and the amino acid to form a new compound or complex. We expect similar species will be formed in all three cases and we made a more detailed study of the reaction with L-methionine.

The mass spectrum of the L-methionine and $SrCO_3$ mixture is shown in Figure 4. The dominant peaks are at $m/z = 385$ and 620, and the expanded spectrum around the latter peak is included in the figure. The three peaks at $m/z = 618.94$, 619.44 and 619.94 are in the intensity ratio for strontium isotopes and the half integer difference indicates the species is doubly

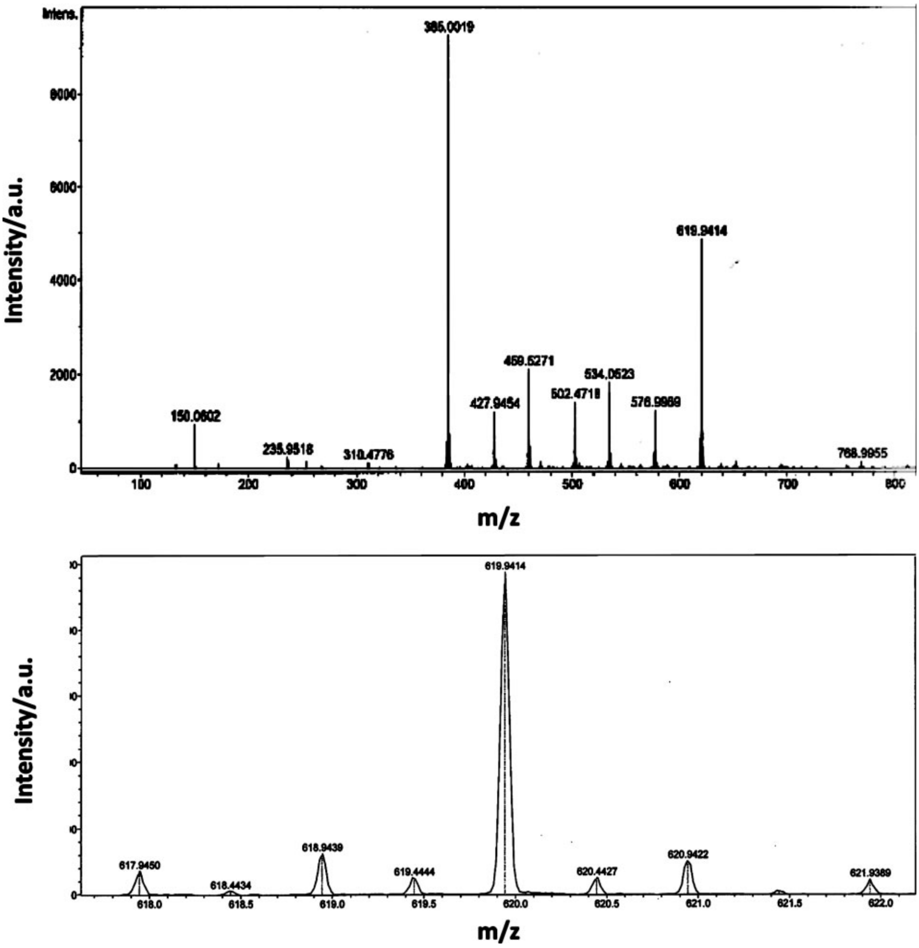

Figure 4.
The mass spectrum of the L-methionine and nanoparticle $SrCO_3$ mixture after 28 days. Upper plot is the whole spectrum, the lower plot is an expanded spectrum around m/z = 620.

charges. An almost identical spectrum to Figure 4 was produced from a 1:1 molar mixture of strontium chloride and L-methionine in water and the solution yielded a crystalline product on evaporation to dryness.

Although the mass spectroscopy results show, a complex forms between the amino acids and strontium it is difficult to deduce structure(s) for the compound as decomposition and breakdown can occur in the spectrometer, i.e. in the ionization chamber and flight tube. Thus, although the peaks at $m/z = 385$ and 620 in Figure 4 can be assigned to complexes containing $(\text{Methionine})_2\text{SrH}^+$ and $(\text{Methionine})_6\text{Sr}_4{}^{2+}$ it is not clear whether these arise from individual complexes or from the breakdown of a larger macromolecular complex. In addition, there is no information on the nature of the counter-ion.

There have been extensive studies[25,26] of the complexes formed between metal ions and amino acids due the importance in biology; however reported work on complexes with strontium is sparse. The amino acids can act as ligands and bind to the metal ion *via* the carboxylate ($-COO^-$), the amine ($-NH_2$) or the sulfur (-S-). The nature of the binding group on the amino acid depends on the metal (hard or soft). Water molecules may also coordinate to the metal in addition to the amino acid. An extended, polymer-like complex has been reported[27] from a reaction of strontium chloride and an amino acid derivative in water. Similar complexes may be forming in the present study and more work is required to resolve this point.

Conclusion

The current work provides more information the reactions of nanoparticle $SrCO_3$ and sulfur compounds that are present in water-logged archaeological wood. This provides a better understanding on how treatment of timbers, like the *Mary Rose* wood, not only neutralises sulfuric acid but also lowers the concentration of reduced sulfur species.[7] The reactions with nanoparticle $SrCO_3$ in the current experiments can be summarised as follows:-

1. Natrojarosite slowly converts to strontium sulfate (and presumably iron carbonate and possibly oxides).
2. There was no measurable reaction with sulfur over the time-scale of the current experiments (28 days).
3. Pyrite slowly converts to iron carbonate. This reaction could be much faster when the $SrCO_3$ is in an excess.
4. Complexes containing strontium ions are formed with amino acids; however more work is required to determine their structure and composition.

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