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Saturated salt solutions in showcases: humidity control and pollutant absorption

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Abstract

The sustainable, passive climatisation of display cases using saturated salt solutions is rarely applied nowadays. These solutions adjust the atmospheric humidity to the specific deliquescence relative humidity (DRH) of the salt. Practical problems like the risk of spilling or 'creeping' of salts can be overcome. The DRH of suitable salts does not depend significantly on temperature. Solutions were Oddy-tested to check for corrosive emissions of the acids corresponding to the salt anions. Only magnesium chloride failed in accordance with thermodynamic calculations of the HCl vapour pressure. Solutions can absorb water-soluble pollutants like acids or aldehydes from the atmosphere, as has successfully been demonstrated for formaldehyde in chamber experiments. The alkaline potassium carbonate solution not only dissolves acids and aldehydes but also reacts with them chemically. Research needs to further study the absorption of pollutants are outlined. A revival of the saturated salt solution would make museum displays more sustainable.

Keywords: Museum display cases, Formaldehyde, Oddy test, Pollutants, Potassium carbonate, Relative humidity, Saturated salt solutions

Introduction: salt solutions for sustainable cabinet climatisation

Heating, ventilation, and air conditioning (HVAC) system suppliers and cabinet makers offer energy consuming electric (de-)humidification devices for museum rooms and display cases. However, these depend on a defect-free run of machines and sensors and an uninterrupted power supply. While these systems are (nearly) perfect in stabilising the relative humidity (RH) in the short run, it is very likely that they will fail at least once over decades. And the total risk to exhibits because of mechanical damage (cracks, delamination, etc.) 'is dominated by the one bad event', not by fluctuations of lower amplitude [1, p. 29]. Is that sustainable?

There is a passive, more sustainable alternative for closed display cases: saturated salt solutions. Dissolved salts lower the water activity in solution and, in equilibrium with the atmosphere, the vapour pressure of H₂O

and, therefore, the RH. Depending on the RH of the air, a saturated solution with added solid salt can either dehumidify or humidify the surrounding atmosphere and will maintain its specific deliquescence relative humidity (DRH). Such mixtures of solid salt and saturated solution are routinely used in science to adjust the RH in small enclosures, e.g., to calibrate hygrometers. The standard ISO 483:2005 describes their use for the measurement of plastics at constant RH. As pioneer, the Viking Ship Museum in Oslo used calcium nitrate solutions for the display of sensitive archaeological wood carvings since 1957 [2]. The whole maintenance requirement was to add some distilled water during the heating period once a year [3]. This is a major advantage over silica gel, which needs re-conditioning to a desired RH. Some other museums worldwide followed, and the method is shortly described in standard textbooks on museum technique [4–6].

Unfortunately, saturated salt solutions have become a little out of fashion nowadays. In Germany, for example, museum display case makers do not offer specially designed cases any longer. Internationally, there

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is nearly no new literature after 1991 on the use of saturated salt solutions in museums and just two websites with some practical advice [7, 8].

To inspire new interest in this old method, this contribution discusses practical problems of application found in the literature, collects data on the thermal variation of the DRH, and investigates corrosive emissions of corresponding acids by the Oddy test and thermodynamic calculations. Physicochemical considerations lead to the novel idea that such solutions absorb pollutants from the showcase atmosphere. This will be checked experimentally for formaldehyde as an example.

Experimental

Corrosivity

The corrosivity of materials by emission of harmful vapours in display cases is routinely checked by the Oddy test. The usual 2 g of test material and water in a separate vial in the standard protocol were replaced by 5 g of salt (all Merck, reagent grade) sprinkled with 0.5 mL deionised water in the reagent tubes. At all temperatures, this will guarantee that the solutions formed are saturated. All other details followed the latest experimental procedure of the British Museum [9] representing the largest experience worldwide. Pure (99.99%) copper, silver, and lead coupons were exposed at 60 °C for four weeks to the atmosphere over the saturated salt solutions and then visually evaluated for signs of corrosion.

Formaldehyde absorption

A glass test chamber (1 m³) was used under static conditions (no air flow). The open plastic tray for the salt solution measured 47 cm × 37 cm × 10 cm. After achieving the DRH in the chamber, the initial concentration (104 µg/m³ for K₂CO₃, 130 µg/m³ for Mg(NO₃)₂·6H₂O) was adjusted by dosage of a formaldehyde test gas (Linde, 19.9 ppm, 500 mL/min). To check for reproducibility, another H₂CO dosage followed after ca. 6–7 h when the remaining formaldehyde concentration was very low. The formaldehyde concentration was measured continuously with a Gasera one formaldehyde monitor (Fa. Gasera), detection limit < 1 ppb.

The use of salt solutions in museums

Spillage and salt deposition

A major general argument against the use of a liquid is that it can be spilled. However, this risk can be minimised by having only trained conservators handle the solution containers and placing the trays at the bottom of the case. Containers can be covered with a tightly fitted water permeable membrane (e.g., Gore-Tex), as described by Creahan [10].

Some time is needed to reach the desired RH in large cases; therefore, a large solution surface is desirable. A fan can be used if needed to avoid a humidity gradient in high, non-tight display cases. Coverage of the container with a permeable membrane avoids the formation of any salt spray by fans that are too strong. Alternatively, a silica gel sheet (e.g., PROSORB) can be used in the tandem climatisation to cover the container according to Waller [7]. This allows a quick response to RH changes (e.g., after opening of the case) and adds some additional buffer capacity.

During dry phases, salts are deposited from the solution and tend to ‘creep’ along and over the container walls. This was especially a problem with sodium bromide, as described by Padfield [11]. However, sodium bromide should no longer be used because it can form the very reactive chemical bromine in the solution [12] that can evaporate. ‘Creeping’ can be overcome by using hydrophobic containers (e.g., polyethylene [13]) or coating the upper walls with paraffin.

Temperature dependence of the DRH

The change in RH caused by temperature changes is a permanent problem in climatisation. The solubility of salts can increase or decrease with increasing temperature; therefore, the DRH of a salt may depend on temperature (Table 1).

The chlorides of calcium and magnesium have similar DRHs, but that of calcium is more temperature dependent. The same holds true for the nitrates. This is an advantage of the magnesium compounds, which are preferable. Their variation is much smaller than the ± 5% RH fluctuation normally accepted for museum climates.

The DRH of potassium carbonate (‘potash’), hitherto not applied in museums, is absolutely stable. It does not vary with temperature at all (a conservator’s dream!).

Harmful emissions from salt solutions?

In the literature, some concerns on the stability and corrosivity of salt solutions can be found but are not

Table 1 DRH of relevant salts at various temperatures

| Chemical name | Formula | 15 °C | 20 °C | 25 °C |
|--------------------------------|--|-------|-------|-------|
| Calcium chloride hexahydrate | CaCl ₂ ·6H ₂ O | 28.1% | 30.9% | 34.1% |
| Magnesium chloride hexahydrate | MgCl ₂ ·6H ₂ O | 33.3% | 33.1% | 32.8% |
| Potassium carbonate | K ₂ CO ₃ | 43.2% | 43.2% | 43.2% |
| Magnesium nitrate hexahydrate | Mg(NO ₃) ₂ ·6H ₂ O | 55.9% | 54.4% | 52.9% |
| Calcium nitrate tetrahydrate | Ca(NO ₃) ₂ ·4H ₂ O | 56.9% | 53.7% | 50.7% |

Data taken from Greenspan [14], for the calcium salts calculated from Wexler [15]

specified clearly. Piechota [16] wrote, ‘Some salts degrade over time to such an extent that they can emit measurable quantities of gaseous pollutants.’ Hilbert [6, p. 161] warned that ‘the extremely low, but not neglectable vapour pressure of the salt [*sic*] may lead to condensation and corrosion phenomena in the long run.’ Twilley [12] ‘was concerned with the theoretical possibility of the evolution of acidic volatiles within the enclosed case due to chemical reactions within the saturated solution.’

It is not the salt itself but the corresponding acid of the anion that might cause problems. Nitric acid (HNO_3) and hydrochloric acid (HCl) are strong meaning they are nearly fully dissociated in aqueous solution. However, traces of the free undissociated acids will be present in solutions of their salts in equilibrium. Some of that traces of acid will evaporate into the atmosphere.

The corrosivity of materials in display cases is routinely checked by the Oddy test [9]. Saturated salt solutions for use in cases should, of course, also be tested. The potassium and magnesium salts in Table 1 were selected for a modified test (see 2 Experimental). Potassium carbonate and magnesium nitrate hexahydrate passed the Oddy test (no corrosion on Cu, Ag, and Pb coupons after 4 weeks at 60 °C). Magnesium chloride hexahydrate caused clear corrosion on copper despite its relatively low RH (33% at 25 °C, 29% at 60 °C) and, therefore, failed the Oddy test. Consequently, it should generally not be used in display cases. This certainly holds true for metal exhibits. However, magnesium chloride hexahydrate has been used over three decades for the display of ‘sick glass’ at the Augustiner Museum Freiburg [7] and the Veste Coburg (Fig. 1) with good results, the sensitive glasses appear to be stable at this DRH. This points to another possibility: Are traces of acid in the atmosphere here even beneficial? Could they neutralise some of the alkalinity on the glass surface, which attacks the silicate network (the cause of ‘glass sickness’)? This will need further study.

Thermodynamic calculations are in accordance with the Oddy test results. The acid vapour pressure over saturated salt solutions can be estimated from thermodynamic models, which include the relevant ions [17]. A calculator is freely available online [18]. A saturated magnesium chloride solution is in equilibrium with ca. 23 ppb HCl in the atmosphere. This is more than two orders of magnitude more than the background level of HCl indoors (0.05–0.20 ppb; [19, p. 81]). Iron is the metal most sensitive to HCl, and indeed, there is anecdotal evidence for the corrosion of ferrous armatures in such cases despite the low RH. And the sensitivity of copper to traces of HCl is known from literature: a Cu-coated wafer exposed to a similar HCl concentration showed clear signs of oxidation after 65 h at a RH < 1% [20, p. 3–4,



Fig. 1 Display case for ‘sick’ glass at Veste Coburg using magnesium chloride solution in plastic containers in the lower part during maintenance. © H. Grieb

Fig. 2] compared with a reference sample under clean-room conditions at 40% RH.

For magnesium nitrate, less than 0.2 ppb HNO_3 in the atmosphere are in equilibrium with a saturated solution. For comparison, indoor measurements in a non-airconditioned museum in LA found 0.6 ppb on average [21], peak and outdoor levels were much higher. The background concentration of NO_2 as its precursor in atmospheric chemistry is at least 5 ppb minimum indoors [22], so a small contribution from the nitrate solution might not be relevant. For the similar calcium nitrate, no corrosion has been observed in 30 years of use on excavated iron and copper alloys in the same display case [3].

The equilibrium pressure of carbon dioxide over K_2CO_3 (some 3 ppb) is five orders of magnitude lower than the current carbon dioxide content in the atmosphere of ca. 410 ppm (=410,000 ppb). This means that carbon dioxide (like other acid gases, see below) will be taken up by the solution and not emitted. The use of K_2CO_3 is absolutely safe in terms of corrosivity.

Salt solutions as pollutant absorbers

Atmospheric pollutants are still a problem in museum displays, and the search for well-suited absorbing materials is ongoing [23]. It was found that ‘the assumption that silica gels, which are installed in display cases to buffer relative humidity, might also act as pollutant adsorbers cannot be confirmed’ [23, p. 13].

So far, despite their potential, the use of aqueous solutions as absorbers in display cases has never been discussed or tested experimentally. According to Henry’s law, gas molecules in the atmosphere are in equilibrium with gas dissolved in a solution. Therefore, the atmospheric pollutant concentration in a closed case will generally be lowered when an aqueous phase is present. In

other words: aqueous solutions are expected to absorb pollutants from the showcase atmosphere and thus ‘clean’ the air.

Acid gases

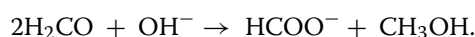
Acid gases like NO_x , SO_2 , HCl , formic acid, and acetic acid pose a major problem in displays. Adsorbing materials like active charcoal will physisorb them [23]. Under high load, a re-desorption into the atmosphere is theoretically possible but has not yet been proven in museum applications.

Potassium carbonate has an important special advantage: As every carbonate solution, it reacts as a base, the pH of a saturated solution is ca. 11.3. Such basic solutions act as a sink for acid gases because these pollutants react to the respective anions at a high pH. Acid gases are neutralised in the solution.

The same holds true for the most relevant reduced sulphur pollutants. Hydrogen sulfide is a weak acid and forms HS^- in solution at a $\text{pH} > 7$. Carbonyl sulfide (e.g., emitted from wool) will hydrolyse to carbon dioxide and hydrogen sulfide in the solution and, consequently, also form HS^- at the given pH.

Aldehydes

Formaldehyde and other aldehydes are reactive pollutants. Recent research at the Institute of Conservation Sciences in Stuttgart [24] showed the relevance of formaldehyde in glass-induced metal corrosion on museum exhibits (GIMME). Formates dominate as copper corrosion products [24]; otherwise (no glass contact), they are very rare on copper alloys [25]. This can be explained by the direct Cannizzaro reaction of formaldehyde (CH_2O) to formate in an alkaline medium (provided by glass deterioration):



What happens in surface films on glass will also happen in a saturated carbonate solution: aldehydes are absorbed and annihilated by a chemical reaction to the non-volatile formate ion and non-corrosive methanol.

In GIMME model experiments, the glass contact was simulated by impregnation of metal coupons by dipping in a 1 mol/L alkali carbonate solution and drying. These coupons were then exposed to formaldehyde vapours in desiccators. The first visible occurrence of glass-induced metal corrosion could be slowed down considerably when magnesium chloride or potassium carbonate solutions were present. The reduced humidity (33% for magnesium chloride) and also the chemical removal of aldehydes by potash might be relevant.

This was checked experimentally (for details see 2 Experimental) at the Fraunhofer Wilhelm-Klauditz-Institute for

Wood Research, Braunschweig/Germany. Their division ‘Materials Analysis and Indoor Chemistry’ is recognised for its expertise on pollutants in museums, libraries, and archives and published a textbook [26]. A concentrated solution of potassium carbonate ($\text{RH} = 43\%$) was exposed to an initial formaldehyde concentration of $104 \mu\text{g}/\text{m}^3$ and one of magnesium nitrate ($\text{RH} = 53\%$) to $130 \mu\text{g}/\text{m}^3$ in emission test chambers (1 m^3 volume). In opposite to a blind test (no solution in the chamber), the formaldehyde concentration in the air declined rapidly for both. However, for potassium carbonate, the initial peak formaldehyde concentration in the atmosphere was halved in only 20 min, while it took 50 min for magnesium nitrate (and 47 min respectively 107 min to get down to $\frac{1}{4}$).

These experiments demonstrated the potential of salt solutions to absorb pollutants and thereby ‘clean’ the display case atmosphere. Thus, the theoretical expectation from Henry’s law was proven for this case. The faster performance of potassium carbonate may point to a chemical contribution (pH, Cannizzaro) to the physical absorption as discussed.

Outlook: open questions

The expected promising ability of saturated solutions of K_2CO_3 (43%) and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (54%) to absorb pollutants should be checked in detail for all relevant pollutants (see above, including H_2S) in typical concentrations. The reduced pollutant levels that can be achieved in the long run can be compared with NOAELs (= no observed adverse effect level [27]) and data for other absorbents in the literature. It will be interesting to see if the basic solution of K_2CO_3 has advantages by reaction with acid gases and aldehydes compared with only the physical dissolution of pollutants by the neutral magnesium nitrate.

Although potassium carbonate is recommended in ISO 483:2005 for laboratory use, it appears to be a new material in museum climatisation. Therefore, practical experience with potassium carbonate in showcases needs to be collected. Open questions to be watched in museum applications are:

- RH: How fast is the equilibration of the RH after opening of cases? Can the desired RH be reached in cases that are not 100% tight, or is there still an influence of the ambient climate and a humidity gradient depending on the geometry of the case (fan needed?)?
- Solution behaviour: Will the upper solution layer get diluted upon dehumidification yielding a higher RH [8] (as observed with magnesium chloride)? Are inhibiting salt crusts formed on the solution during dry periods outside? What are sufficient maintenance

intervals (e.g., adding distilled water during dry periods)?

- Container: What is the optimal container design (capacity, material to avoid creeping, anti-spill cover, transparency)?

If potassium carbonate and magnesium nitrate behave similarly, their choice should be governed by the desired RH for the display case. If potassium carbonate proves to be superior, it can be recommended for general museum use. Its DRH of 43% is low but still in the general range of 40–60% RH recommended for mixed collections [1] and acceptable for many materials. It is highly recommended when a drier storage is needed. Where hitherto the corrosive magnesium chloride has been used (e.g., for ‘sick’ glasses), the replacement by potassium carbonate should be considered when metal objects are present. In contrast to magnesium chloride (DRH = 33%), the DRH of potassium carbonate is above the safety limit for crack formation (‘crizzling’) in gel layers on glass assumed to be somewhere between 35 and 42% in most of the literature [28, p. 54].

Conclusion

Saturated salt solutions can be used for the passive control of RH in display cases. First applications date back to the 1950s. The DRH of magnesium nitrate (54%) and potassium carbonate (43%) is nearly independent of the outside temperature. Both salt solutions pass the Oddy test, they are not corrosive to objects. The calculated vapour pressure of nitric acid over the nitrate solution is indeed very low. In general, salt solutions have a hitherto overlooked advantage: They absorb pollutants from the display case atmosphere. Gas chamber experiments with formaldehyde as an example gave excellent results, formaldehyde was quickly absorbed. The alkaline solution of potassium carbonate has the advantage to not only absorb, but also to neutralise acid pollutants and to react with aldehydes. This chemical prediction should be explored in further studies.

As passive climatisation, salt solutions do not depend on the defect-free performance of active HVAC systems. This is a major advantage for risk management in museums, severe damage to objects by malfunction of such systems can be prevented. And much permanent energy consumption could simply be avoided by passive systems. This would lower the carbon footprint for display climatisation considerably and make it more sustainable on a global level.

Therefore, this contribution is meant to inspire new interest in the application of saturated salt solutions, a well deserved revival.

Abbreviations

ACCENT: Atmospheric composition change: the European network of excellence; DRH: Deliquescence relative humidity; HVAC: Heating, ventilation and air conditioning; ISO: International Organization for Standardization; RH: Relative humidity.

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Author contributions

GE designed the project, collected all information and wrote the manuscript. The author read and approved the final manuscript.

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Availability of data and materials

All data are available from the author on reasonable request.

Declarations

Competing interests

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