

# The evaluation of zinc hydroxychloride cement pastes for the conservation of damaged tiles

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## **ABSTRACT**

This study examines the potential of zinc hydroxychloride cement pastes as a fill material for the conservation of damaged historic tiles. The scope for modifying various properties was investigated by the preparation of numerous versions of the basic formulation in which the ratio of the three principal constituents – zinc oxide powder, an aqueous solution of zinc chloride, and a mineral aggregate – was varied. The importance of adjusting these variables for optimal performance was confirmed. The concentration of the zinc chloride solution was also found to be an important factor as this affected the useful working time before cementation occurred. The resultant reaction products were examined by x-ray diffraction in several cases. Compressive and flexural strength tests were undertaken on a number of the variants and on a commercial formulation (Lithos Arte). Observations of the cement-tile interface (using optical

## **INTRODUCTION**

This paper explores the potential of cement pastes based on zinc hydroxychloride for the conservation of damaged tiles where disruption to the glaze and ceramic body has occurred, or where sections of the tile are missing. Such damage is, to a greater or lesser extent, present in very many historic tiles both in museum collections and in situ, in their original architectural settings. The damage takes the form of simple losses at the edges of tiles, in many cases due to course dismantling from their original location, or surface and perimeter damage, often as the result of salt efflorescence. This research was motivated by the lack of suitable fill materials for tiles in the Netherlands and Portugal, in internal and external architectural settings, respectively. The scale and scope of tile production in the Netherlands in the 17th and 18th centuries, both for the domestic market and for export, is well documented (van Dam 1988) and the importance of tile-making in Portugal from the 16th century onwards has been concisely summarised by Vaz, Pires and Carvalho (2008). Both countries have, in addition to many instances of collections with single problematic tiles, numerous examples of architectural tile arrays with extensive damage (see, for example, Figures 1–2). The need to identify optimal fill materials for tile collections worldwide is therefore well represented by the acutely problematic issues of these Dutch and Portuguese situations.

For restoration of the damaged areas, suitable fillers must display a range of properties which pertain to the material's working behaviour, physico-chemical parameters, aesthetic appearance and durability. When allied to issues such as cost and availability, it is difficult to achieve an optimal blend of all these features in one material. Furthermore, for tiles in situ, as opposed to dismantled tiles in a museum display, environmental parameters and, especially, hygric properties and the danger of salt crystallisation, place even more stringent demands on the selection of an appropriate fill material. As Durbin states (2005), 'Ceramic conservators have many options of filler pastes available for use with...ceramics at their disposal; however, they are not all suitable for in-situ repairs on architectural schemes.' Needless to say, the threat to the durability of restored tiles exposed on exterior facades is even greater than that for tiles in architectural settings indoors. At present, the most commonly adopted fill materials are organic polymers (especially epoxy, polyester and acrylic formulations), plaster

and scanning electron microscopy) were made. In addition, adhesion was assessed by means of a shear stress test.



**Figure 1**

End section of an array of approximately 260 Dutch tiles (mid-17th century) removed from its original interior location in the 19th century and installed in the Philips Wing of the Rijksmuseum, Amsterdam. The scene, representing the Battle of Downs in 1639, flanked by two polychrome lions, shows areas of loss and damage where an optimal fill material is required. Photo: Nicolas Verhulst

**Figure 2**

Section of an array of Portuguese tiles (second half of 18th century) from the garden setting of Quinta dos Azulejos, Lisbon, showing areas of damage where an optimal fill material is required. Photo: Sílvia Pereira

of Paris and lime mortar (Buys and Oakley 1993), all of which have drawbacks. Disadvantages of these materials include the severe yellowing of most epoxy resins, the water sensitivity of plaster of Paris and the slow cementation process of lime mortars. Since this area of conservation is a challenging example of loss compensation which is still insufficiently researched, the present investigation aims to extend the range of suitable fill materials for the conservation of tiles by consideration of an interesting new option: zinc hydroxychloride cement.

## ZINC HYDROXYCHLORIDE

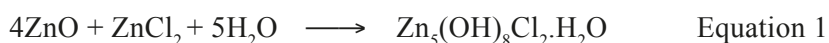
The material which is the subject of this paper, zinc hydroxychloride cement, was first described by Sorel (1855, 784), who claimed it to be '*aussi dur que du marbre; le froid, l'humidité et même l'eau bouillante sont sans action sur ce ciment*' (hard as marble; cold, humidity and even boiling water do not affect this cement).

An interesting initial application of zinc hydroxychloride was its use as a dental cement, but it was subsequently introduced as a stone mortar and repair material, especially in France, Belgium and the Netherlands. For reasons which are not clear, it fell somewhat out of favour for much of the second half of the 20th century. A commercial product based on this formulation is marketed as Lithos Arte and is currently finding a role as a filler and mortar for stone conservation (Anon 2013a).

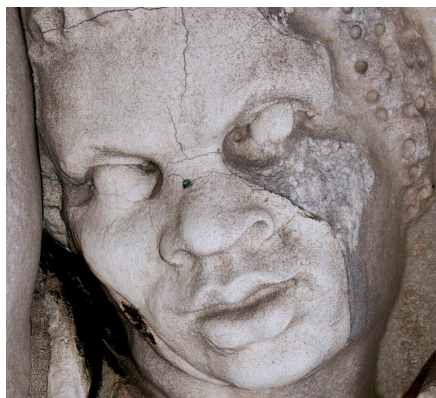
The cement is formed by an acid-base reaction between powdered zinc oxide and an aqueous solution of zinc chloride. The resulting complex, non-homogeneous cement consists of a number of phases, some of which are crystalline and have been characterised. For use as a mortar and conservation repair material, powdered calcium carbonate is the most common aggregate.

Cements based on zinc hydroxychloride (also referred to as zinc oxychloride and, colloquially, as *ciment métallique*) have been well described by Wilson and Nicholson (1993, 283–306), who report the results of the principal scientific studies undertaken to elucidate the reactions taking place and the products formed various oxysalts, including zinc and magnesium variants. On mixing zinc oxide and an aqueous solution of zinc chloride, cementation occurs reasonably rapidly (within 30 minutes) and in significantly shorter time than does the development of crystalline phases, which may take several weeks to form.

A principle product is  $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ , with a 4:1:5 stoichiometry of reagents (Equation 1). This crystalline material occurs naturally as the mineral simonkolleite.



Several authors have discussed the chemistry underlying the formation of zinc hydroxychloride cements and many different compounds in the resultant cement have been proposed. Sorrell (1997) noted that many early studies lack the support of x-ray diffraction characterization. Sorrell himself identified the formation of two different ternary phases as  $4\text{Zn}(\text{OH})_2 \cdot \text{ZnCl}_2 \cdot 5\text{H}_2\text{O}$  (4:1:5) and as  $\text{Zn}(\text{OH})_2 \cdot \text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$  (1:1:2). He also observed, however,



**Figure 3**

Zinc hydroxychloride/calcium carbonate cement paste applied in 1915 to restore the face of one of the marble figures from the tympanum of the Royal Palace in the Dam Square, Amsterdam.

Photo: Lisya Bicaci

that addition of water to the 1:1:2 phase will cause its rapid transformation to the 4:1:5 phase. Interestingly, Sorrell reported that less concentrated solutions lead to a mixture of different phases and that such mixtures often lack workable consistency or suitable working time. Indeed, he found that the setting time of the cements decreases with higher concentrations of  $\text{ZnCl}_2$  until the mixture sets too fast to mix it properly. He also noted that mixtures with too little  $\text{ZnO}$  do not dry out.

Sorrell's research focused on the characterization of the crystalline phases within the mixture, while Nicholson and Tibaldi (1992), in particular, drew attention to the importance of the formation of an amorphous phase as part of the solidification process. As mentioned above, the crystallization of zinc hydroxy compounds occurs at a slower rate than the initial setting of the cement, indicating that crystallization occurs within an amorphous phase. In their study on the very similar zinc oxide/zinc nitrate cement, Nicholson and Tibaldi (1992) concluded that the amorphous phase seems essential for the cement's properties. Furthermore, the powder/liquid ratio and the concentration of the aqueous solution of zinc nitrate were important factors which influence both setting time and compressive strength.

Although these studies do much to elucidate the chemistry behind the formation of the cement from the two main compounds, very little research has considered the cement in combination with aggregates. The lack of conservation science assessments is remarkable; the study by Moens and de Witte (2000) is a rare example. Their report summarises some of the results of a more extensive, unpublished study. While the work of Moens and de Witte is an excellent starting point for further conservation research, it seems likely that these authors may have underestimated the importance of the dual role played by the crystalline and amorphous phases in achieving optimal performance.

Finally, documentary reports on the use and long-term durability of zinc hydroxychloride cements are scanty and so the results of one of the earliest documented restoration campaigns involving this zinc-based cement – the marble tympanum of the Royal Palace in the Dam Square, Amsterdam – are important. In 1915, because of degradation of the marble, this material was extensively used for filling small lacunae and for remodelling major components, such as complete heads, of the tympanum figures and ancillary items. As a result, a large proportion of the marble tympanum now actually consists of zinc hydroxychloride cement. After a century, the durability of the repairs (see for example, Figure 3) has been shown to be remarkably good (Tennent et al. 2013).

## EXPERIMENTAL APPROACH

For a suitable fill material for damaged tiles, the following properties need to be explored: working time; setting time; full curing time; adhesive, compressive and flexural strength; hardness; pore size distribution; durability and negative side effects. For zinc hydroxychloride cement pastes, all these features can be affected by variations in the proportions of the formulation components and the nature of the aggregate. The experimentation reported in this paper sought to explore many but not all of these topics in a pilot



investigation. The assessment is therefore not comprehensive; porosity, hardness and durability are additional important topics which will be addressed in future studies together with a more comprehensive assessment of all properties. It was the intention of this first phase of the research to assess the scope for preparation of formulations with the versatility to meet several basic selection criteria for a tile repair material, namely, good workability combined with acceptable adhesive, compressive and flexural strength.

## RESULTS AND DISCUSSION

### Workability

An investigation of the workability of the cement paste formulations with and without aggregates was a prime goal of the preliminary experimental research carried out at West Dean College and the University of Amsterdam (Oliveira 2012, Overhoff 2013). It was recognised at the outset that, in contrast to lime mortar, filled zinc hydroxychloride formulations have the advantage of speed of cementation. Indeed it was deemed a disadvantage that the components tend to react too rapidly. It was felt that it would be helpful to be able to have a clearer understanding of the factors which can prolong the useful working life during which the paste can be applied before cementation takes place. Experiments were conducted to gain information on the relationship between the raw materials and workability. The following parameters were varied: the molar ratio of  $\text{ZnCl}_2/\text{ZnO}$ ; the amount of water in the mixture (i.e. the concentration of the  $\text{ZnCl}_2$  solution); the nature and quantity of the aggregates in the mixture ( $\text{CaCO}_3$  and  $\text{SiO}_2$ ). The general method of preparation involved first mixing the dry ingredients, using a wooden spatula, followed by addition of an aqueous solution of zinc chloride. The well-mixed paste was transferred to a polypropylene test container and left to set.

More than 50 different variants were prepared in order to gain an impression of the subtle interplay of variations in the different parameters. More extensive experimentation is required in order to quantify more precisely the relationships between the components of the filled pastes and the workability of the mix, but results of this investigation may be summarised as follows:

- The mixture should provide a surplus of ZnO. (A deficiency in ZnO gave unstable cement pastes which are generally unacceptably slow to dry out whilst the amount of ZnO did not appear to affect the setting rate or workability as long as it exceeded that of  $\text{ZnCl}_2$ .)
- The powder/liquid ratio should be in the range 2/1–3/1.
- The amount of water in the mixture greatly influences the setting. (A cement paste with a 10% aqueous solution, by mass, of  $\text{ZnCl}_2$  will set much more slowly – in about twice the time – than a cement paste made with a 25% aqueous solution of  $\text{ZnCl}_2$ . 25% solutions of  $\text{ZnCl}_2$  formed simonkolleite, identified by XRD, within 5 days whereas <10% solutions of  $\text{ZnCl}_2$  showed no simonkolleite formation after 5 days although it had begun to form after 14 days.)

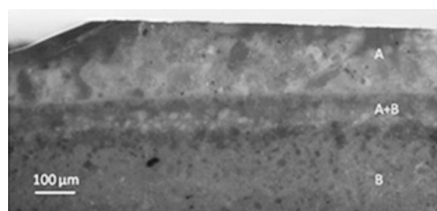


Figure 4

Cross section of ceramic replica coated with Lithos Arte liquid component prior to application of the cement paste. A = ceramic paste, B = ceramic, A + B = penetration of paste into the ceramic

Table 1

Results of shear strength tests

Shear strength (MPa)	
Lithos Arte® on ceramic replica	0.69 ± 0.11
Lime-quartz mix on ceramic replica	0.10 ± 0.05
Lithos Arte® on ceramic replica with liquid component coating	0.71 ± 0.29
Lithos Arte® on ceramic replica with Paraloid® B-72 coating	0.09 ± 0.01
Lithos Arte® on historic tile with liquid component coating	0.73 ± 0.36

- Calcium carbonate in the mixture gives the mixture a more clay-like consistency.
- The final structure of the cement paste can be adapted by the grain-size of the aggregate.
- Too much calcium carbonate causes shrinkage and too much silica causes extreme shrinkage of the cement paste. (Blends of the two aggregates seem to be advantageous, compared to either alone.)

### Shear, compressive and flexural strength

Experiments were performed to assess the behaviour of certain formulations under load. Firstly, shear strength experiments were performed using a standard testing set-up, namely a 50-kN dual column Trinius Olsen H50kS apparatus, performed on sample cubes comprising Lithos Arte cement paste applied to a tile substrate. The cement was held fast and pressure was applied to the ceramic half. The results, based on six replicates, are given in Table 1. There is consistency in the values obtained for the three tests in which Lithos Arte was applied to a historic tile or a specially fired tile corresponding to a historic Portuguese composition. Interestingly, prior application of the zinc chloride liquid component to the substrate surface, as recommended for adhesion promotion, had no clear beneficial result in these tests, although penetration of the cement into the tile was visible (Figure 4). Application of a coating of the Paraloid B-72 (10% in acetone) caused a significant decrease in shear strength to a level comparable to lime mortar. (All tests were conducted 10–14 days after preparation of the samples and so all results, especially those for the lime/quartz mortar, represent values at this stage in their development.)

The values obtained for the compressive strength and flexural strength (MPa) (Table 2) were conducted on a simple compression apparatus on samples area of 40 × 40 mm and, for flexural strength, on an Instron universal testing apparatus with an applied force at a speed of 0.05 mm/sec. The results for the former are given by Equation 2, where F is the load applied at rupture (N), A (m<sup>2</sup>) is the area of the sample cube side.

$$\sigma = \frac{F}{A} \quad \text{Equation 2}$$

Table 2

Results of compression and flexural strength tests

Sample	ZnCl <sub>2</sub> (g)	H <sub>2</sub> O (g)	ZnO (g)	CaCO <sub>3</sub> (g)	SiO <sub>2</sub> (g)	S <sub>(compression)</sub> (MPa)	S <sub>(flexural)</sub> (MPa)
1	50.0	150.0	90.34	270.0	-	4.90 ± 0.41	1.31 ± 0.23
2	50.0	150.0	90.34	135.0	115.0	3.55 ± 1.08	2.73 ± 1.42
3	20.0	180.0	35.81	230.0	200.0	1.58 ± 0.22	1.03 ± 0.34
4	50.0	150.0	90.34	135.0	145.0 (coarse)	6.02 ± 1.89	1.77 ± 0.58

For a rectangular sample under a load in a three-point bending setup the flexural stress (MPa) is given by Equation 3, where F is the load at rupture (N), L is the length (m), b is the breadth (m) and d is the depth (m) of the sample.

$$\sigma = \frac{3FL}{2bd^2} \quad \text{Equation 3}$$

Three replicate samples were tested for each composition. The results show a relatively high variance. It was difficult to prepare samples of the large dimensions ( $40 \times 40 \times 160$  mm) required for the tests without introducing varying amounts of porosity. Thus the values obtained are likely to be lower than those for the relatively smaller amounts of material used for filling tile lacunae. Interestingly, sample 3, which had set without simonkolleite formation, had lower compressive and flexural strengths. Furthermore, although it was difficult to prepare uniform samples, the results confirm that aggregates play a role in determining the resultant mechanical properties of different formulations.

## CONCLUSIONS

This investigation has established the potential of zinc hydroxychloride cement pastes with added aggregates for the conservation of damaged tiles. Two cultural contexts for historic tiles, indoor settings in the Netherlands and in exterior facades in Portugal, provided the framework for an initial assessment of some of the relevant attributes which need to be established for selection of a new fill material for tiles. This research has demonstrated the inherent virtues of zinc hydroxychloride cement pastes and has shown that there is scope to develop different formulations which modify and optimise working behaviour and physico-chemical properties in order to fulfil different requirements. The research has underscored the complex and incompletely understood chemistry of the acid-base cement-forming reaction of zinc oxide and zinc chloride and the added complexity brought about by the inclusion of aggregates in the mix. On the other hand, the findings of this preliminary phase of the research confirm that this material has virtues which merit deeper investigation, not only for tile conservation but also for other conservation applications. Future studies by the principal authors in Amsterdam and Lisbon will build on this pilot study by consideration of porosity, hardness and durability.

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