

Re-thinking the Approach: Techniques Explored at Winterthur for the Stain Reduction of Ceramics

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Keywords

stain reduction; ceramics; cleaning; chelating agents

Abstract

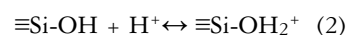
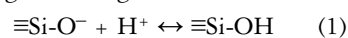
Stain reduction is often required during conservation treatment of ceramics. Although the historical relevance of the stain must first be considered, stains are often disfiguring enough that they limit full aesthetic appreciation of an object. This is particularly true within fine arts collections. For the past several years, the authors have delved deeper into this topic, evaluating current materials and methodologies and applying these concepts during the treatment of dozens of ceramics in the Winterthur collection. In the process, they go beyond what is mentioned in the conservation literature by considering new options and developing a sequence of steps for stain reduction that has provided excellent results. In this paper, the authors discuss cleaning theories and present new techniques and materials, proposing a re-thinking of the approach to stain reduction on ceramics.

Introduction

Knowing the nature of ceramic bodies and how stains are held within them is essential to designing procedures for the reduction of those stains. Ceramics vary in mineral composition, particle size, and ionic exchange potential; also, stains are often mixtures of organic and inorganic constituents. Although the stains are held by a number of forces, including hydrophobic/hydrophilic interaction and specific bonding, electrostatic forces represent a key reason stains are held within ceramic bodies. This paper focuses on how we can control our cleaning systems by adjusting the pH and ionic environment and by targeting (chelating) specific metal ions. Understanding the crucial role that ions play in binding stains to a ceramic structure goes a long way in determining how to desorb them. This can then be followed by (or used in concert with) other standard methods, such as oxidative bleaching, to further affect organic staining materials.

Ceramic Cleaning Theory

The electrostatic net charge on a mineral surface such as a silicate, and the type of ions held or 'sorbed' there, is fundamentally a function of pH. Ion-binding sites are amphoteric: they take on an extra H^+ or lose one to develop either a net positive or negative charge:



At high pH values, the species on the left of equation (1) predominates, and the silicate attracts positively-charged ions from solutions; in an acidic environment, equation (2) predominates, and a silicate surface is positively charged, attracting negatively-charged ions. The 'zero-point' pH (pH_{zpc}) is the pH where positive sites are minimal and equal to the number of negative sites, and the net surface charge is zero. With clay structures such as kaolinite, the pH_{zpc} is 4.6; the pH_{zpc} for montmorillonite is 2.5, for feldspathic minerals it is 2–2.4, and for many silicates it is 2.0 or slightly above. At the pH_{zpc} , interactions between solute ions and the mineral surface are minimised.

When silicates are predominantly negatively charged, polyvalent cations held at the surface can bind other ionic material to them, thus retaining staining compounds, such as weakly acidic organic materials. Particle size contributes to the availability of these charged sites, and most clay minerals have high surface area-to-weight ratios. Because of this, small particles can bind significant amounts of adsorbed molecules at their surface as hydrated species. These are often described as ‘outer sphere’ complexes where the ion remains bound to the hydration shell, not directly to the surface, and attraction is purely electrostatic. The charges at these binding sites are often significantly higher than in the ceramic itself.

Outer-sphere species are held in a manner where they are easily exchanged with ions of a similar charge. Ions adsorbed by outer-sphere complexation in particular diffuse and are readily exchangeable with similar ions in solution.

Generally, for minerals such as silicates or aluminates, whose surface charge is pH-dependent, the amount of sorbed cations increases with increasing pH. Again, this is due to positively-charged surfaces that repel cations at low pH values, while at high pH values, negatively-charged surfaces attract them. Each cation exhibits a relatively narrow range of pH (about 2 units) over which its sorption increases from near 0% to near 100%; this further emphasises the need for careful control of pH during stain reduction.

While stain retention through ionic means is clearly a function of ion type, pH, and binding site availability, other factors influencing solution dynamics are equally important. These include the porosity of the ceramic itself and capillary movement of liquids through the structure, as well as diffusion of active cleaning agents into the ceramic and the movement of staining materials outward. This is where choosing the right materials to apply the solution is important.

Ceramic Stain Reduction in Practice

Keeping these properties in mind, the authors recommend a protocol: first, use a chelator; second, use an oxidising bleach; and, finally, rinse thoroughly. Throughout the process, it is critical to choose materials that provide careful control, minimising negative reactions and the risk of leaving residues behind. The choice of materials for each treatment presents its own challenges, yet the suggested approach proved successful at safely reducing stains on a variety of ceramics.

Step 1: Choosing a Chelator

Because electrostatic forces largely hold stains to a ceramic body, utilising a chelator to target specific metallic components is often the best place to start. A ‘chelate’ is any material with an affinity to bind a divalent metal ion and stay in solution without precipitating.

It is essential to understand that the functionality of any chelator is dependent on the pH of its surrounding solution. Most of the common chelators contain ‘ligands’ or functional groups that are ionisable acid groups. The acid dissociation constant (pK_a) of each acid group present in the chelator structure determines the pH where these groups will be fully charged (usually one pH unit above the group pK_a). Chelation is most effective when at least three groups of the chelator are ionised (pK_3), and the pH value is closer to the pH_{zpc} of the ceramic. Stain removal from ceramics is probably most efficient at pH values close to the pH_{zpc} . Common chelators and their range of pK_a values are listed in table 1. For example, citric acid is already triply ionised at pH 6.4 and is an efficient chelator above that pH.

	Citric acid ¹	EDTA ²	DTPA ³	Tiron ⁴	HBED ⁵
pK_1	3.13	1.99	1.80	-	4
pK_2	4.76	2.67	2.55	-	8
pK_3	6.40	6.16	4.33	7.66(-2)	
pK_4		10.26	8.60	12.60(-3)	
pK_5			10.58		

1. (Dean 1973); 2. Disodium ethylenediaminetetraacetic acid (Dean 1973); 3. Diethylene triamine pentaacetic acid (Dean 1973); 4. 4,5-Dihydroxy-m-benzenedisulfonic acid (Dean 1973); 5. N,N'-Di(2-hydroxybenzyl) ethylenediamine-N,N'-diacetic acid monohydrochloride hydrate (<http://pubchem.ncbi.nlm.nih.gov/summary/summary.cgi?cid=124920> accessed 11/30/2012)

Table 1. Selected acid dissociation constants (pK_a) of various chelators.

A common way to determine the relative strength of a chelating material is to compare the formation constant (pK_f) of the chelator–metal complex to the solubility product (pK_{sp}) of a metallic species. In general, complexation will occur when the pK_f of the complex is greater than the pK_{sp} of a given species. Table 2 demonstrates that, in order to dislodge components of a stain being held (adsorbed) by ceramic bod-

ies, certain chelators will be more effective than others, depending on the metal ions being targeted.

Citric acid, for instance, can effectively desorb organic material being held to a magnesium silicate by outer shell adsorption, as described above. However, if rust is the staining culprit, the pK_{sp} for $Fe(OH)_3$ is 38.5; only a chelator with a pK_f greater than this number will preferentially bind Fe^{+3} ions in

Mineral	pK_d/pK_{sp}	Metal ion	pK_f citric acid ³	pK_f EDTA	pK_f DTPA ⁴	pK_f Tiron	pK_f HBED ^(5,6,7)
Stain Components							
Ca(OH) ₂	5.2	Ca ⁺²	4.7	11.0	10.9	5.8	9.3
CaSO ₄ 2H ₂ O	4.5						
CaCO ₃	8.5						
Mg(OH) ₂	11.2	Mg ⁺²	3.3	8.7	9.0	6.9	
MgCO ₃	5.2						
Al(OH) ₃	32.9	Al ⁺³	14.7	16.1	18.6	31.1	24.8
		Pb ⁺²	6.5	18.0	18.9	18.3	18.2
Fe(OH) ₂	15.1	Fe ⁺²	3.1	14.3	16		
Fe(OH) ₃	38.5	Fe ⁺³	12.5	25.1	27.9	35.9	39.6
Cu(OH) ₂	19.6	Cu ⁺²	4.3	18.8	21.5	23.7	21.4
CuCO ₃	9.86						
Silicates							
CaO nSiO ₂ ¹	7.9						
MgO nSiO ₂ ¹	4.6						
Clay Components							
Pyrophyllites/Talc							
Al ₂ Si ₄ O ₁₀ (OH) ₂ ²	1.0						
Fe(III) ₂ Si ₄ O ₁₀ (OH) ₂ ²	-13.7						
Fe(II) ₃ Si ₄ O ₁₀ (OH) ₂ ²	7.2						
Mg ₃ Si ₄ O ₁₀ (OH) ₂ ²	25.1						
Micas							
KAl ₂ AlSi ₃ O ₁₀ (OH) ₂ ²	16.2						
KFe(III) ₂ AlSi ₃ O ₁₀ (OH) ₂ ²	1.0						
KFe(II) ₃ AlSi ₃ O ₁₀ (OH) ₂ ²	23.4						
KMg ₃ AlSi ₃ O ₁₀ (OH) ₂ ²	42.0						
Celadonites							
KAl _{1.66} Si ₄ O ₁₀ (OH) ₂ ²	6.3						
KFe(III) _{1.66} Si ₄ O ₁₀ (OH) ₂ ²	-6.9						
KFe(II) _{2.5} Si ₄ O ₁₀ (OH) ₂ ²	11.7						
KAl _{2.5} Si ₄ O ₁₀ (OH) ₂ ²	26.9						

1. At 25°C (You and others 2007); 2. (Rodriguez-Clemente and Tardy, eds. 1987); 3. (Ohman and Martin 1994); 4. http://www.akzonobel.com/dissolvine/functions/the_right_chelate/ accessed 11/30/2012; 5. (Taliaferro and Martell 1984); 6. (Martell 1978); 7. (Krokhin and others 2000).

Table 2. Selected solubility products (pK_{sp}) of stain and clay components vs formation constants (pK_f) of chelator–metal complexes (pH 7, 20°C).

the presence of OH^- ions. From table 2, it is clear that only HBED will work to complex Fe^{+3} directly from rust (pK_f 39.6 for Fe^{+3}).

Another important consideration is that some of the chelators have higher pK_f values than the pK_{sp} values of metal-containing components normally present in a ceramic. For example, if $\text{Fe}(\text{OH})_3$ in a ceramic that inherently contained significant amounts of Fe-containing pyrophyllitic structures was treated with HBED, Fe^{+3} would also be removed from the ceramic body (the pK_{sp} for Fe^{+3} in these structures is -13.7). On the other hand, a rust-stained pyrophyllite of the generic form $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$, although free of Fe in the body, may contain soluble Al^{+3} with a low pK_{sp} of 1.0. However, any Al^{+3} bound to HBED would quickly be replaced by Fe^{+3} from the rust, with a higher pK_f than Al^{+3} for the chelator (24.8 vs 39.6). As with any cleaning system, a balance must be struck between targeting staining materials without disrupting the clay bodies themselves. If the ceramic in question suffers condition issues such as particularly low firing or unstable glazes and enamels, then the use of chelators may not be recommended, and water alone may be successful at reducing a stain, particularly if the right poultice material is used. While knowing the composition of the materials present in the object is ideal, analysis is not always possible, and therefore spot tests prior to choosing a chelator are of paramount importance.

The final factor to consider when creating a chelating solution is its ionic strength. Too high a concentration of chelating material in solution (hypertonic to the ceramic) or too low (hypotonic) means that unnecessary physical pressures are brought to the ceramic surface. Hypertonic solutions also flood the ceramic with salts and increase the risk that salts will diffuse deep into the surface, thus disrupting the ceramic body and becoming more challenging to subsequently rinse. The goal of a chelating solution is to be isotonic with the surface, theoretically matching the conductivity of the ceramic (this can be estimated through a simple conductivity measurement).

Because chelate formation is an equilibrium reaction, once a chelator is completely saturated with a metal ion, and at its equilibrium point with dissociated ions, it cannot bind additional ions (Wolbers 2000, pp. 117–118). Therefore, more will be needed to deplete additional ions in a stained ceramic. A better cleaning strategy would be to work with multiple applications of a low isotonic amount of chelator in solution and simply replenish it as needed, rather than work at initially high concentrations of a chelator.

Step 2: Choosing an Oxidising Bleach

As most stains also include organic components, bleaching often becomes a necessary second step in the stain reduction process. Oxidising bleaches function in two ways: chemically altering organic residues (making them more polar on oxidation and therefore more water-soluble), and de-colourising them. In contrast to reducing bleaches, their effect on these residues is permanent. Preliminary testing is essential, as all oxidising bleaches can potentially oxidise metallic components, particularly within low-fired bodies, or cause adverse reactions with unstable enamels, metallic glazes and gilding (Hogan 1998; Buys and Oakley 1993).

The most cited oxidising bleach in ceramic stain reduction is hydrogen peroxide (Olive and Pearson 1975; Buys and Oakley 1993; Navarro 1997; Hogan 1998; Oakley and Jain 2002; Williams 2002). Its oxidation potential is 1.8, higher than chlorine, yet weaker than ozone. Made to a slightly alkaline pH, the bleach is more effective while maintaining a safe range for most ceramic glazes. While hydrogen peroxide is stored at cool temperatures to ensure the reactivity of the solution, it is best applied under warm conditions, as the bleaching potential of the given solution increases with elevated temperatures.

Hydrogen peroxide performs well, either used at lower concentrations ($\sim 5\%$ v/v) for general applications, or progressively at higher concentrations (10–15%) for more stubborn or specific stains. The material is quite reactive and breaks down quickly into water and hydrogen, especially in contact with organic residues. Therefore, its use in controlled poultices to limit penetration is recommended. Otherwise, tide-lines may form as the hydrogen peroxide breaks down to simple water, carrying organic residues with it, re-depositing stains at the surface upon drying. Rinsing with water afterwards can be done only superficially, controlling the amount of time the bleach is active in the ceramic body. An oxidising bleach that the authors prefer is carbamide peroxide, which is a stabilised form of hydrogen peroxide, made by adding an equal molar amount of urea. Its main advantage is its uniformity and increased efficiency at reducing organic stains (Norquest 2008). With carbamide peroxide, bleaching takes longer to occur, since it first breaks down into hydrogen peroxide, then to water and oxygen; the urea component breaks down into carbamic acid, which quickly volatilises into ammonia and carbon dioxide. This allows for a more progressive action, no residues, and better results, as demonstrated by its use in the teeth-whitening industry (Tam 1999).

Concentrations recommended are 3%, 5%, 10%, or exceptionally 20%, although proper precautions must be followed when using higher concentrations.

A group of other oxidising bleaches being tested include perborates and percarbonates, which are also more stable than hydrogen peroxide. Their main advantage is functionality at neutral pHs, but as of now more testing is required before they can be recommended.

Step 3: The Critical Rinsing Phase

Rinsing is crucially important whenever materials from a treatment could remain behind in the ceramic body. Rinsing also becomes critical, yet more difficult, with porous bodies; also, as of now, no easy method exists to evaluate the effectiveness of the rinsing phase.

The most important consideration is what happens to the reagent once it has penetrated into the ceramic body. For instance, is the reagent a stable product? Does it break down over time, and into what?

One example is the difference between ammonium and sodium citrate: both of these deliver a citric acid chelator, yet react differently within the ceramic body if not adequately rinsed. Ammonium citrate breaks down into volatile ammonia and citrate ions, which may be left behind, potentially exposing the body to the pH of citric acid (2.5–3) with future introduction of moisture. Sodium citrate, however, is more stable, and potential residues are stable salts that do not deliquesce into more acidic components. Hydrogen peroxide and carbamide peroxide, especially when used at lower concentrations, will quickly break down, causing no long-term impact. In contrast, most acids and alkalis easily form salts with materials in the ceramic body; these materials could then migrate to the surface and cause significant salt and stability issues. Stability aside, it is essential to minimise any risk of residues by using the lowest concentration of chosen solution possible. If multiple applications, larger volumes of solution, or deep penetration into the ceramic body are required, rinsing becomes even more critical. In a nutshell, best practice is to use lower concentrations, minimise the amount used, and act at the surface as much as possible.

In the chelator–bleach sequence, the latter serves already to rinse chelator residue. This is followed by a final rinse with de-ionised water. If low concentrations of chelator and bleach are utilised, the final rinse need not flood the ceramic and deeply penetrate; rather, smaller quantities of water are effective. Tests show that excessive rinsing with water is risky, as

residual staining materials now affected by the chosen cleaning solutions can be more readily mobilised by water, creating the potential for tidelines and re-deposition of stains.

Another rinsing technique tested is using a DEAE (diethylaminoethyl) cellulose poultice to deliver the rinse water. This material has increased affinity for the ions one hopes to rinse, for instance to draw out remaining citrate anions. Finally, rinsing with a solvent or a solvent/water mixture (e.g. denatured alcohol/water) is being tested. Theoretically, this system can be more effective at clearing remaining citrate ions.

Step 4: Choosing a Poultice System

The most successful technique for stain reduction is through the use of a poultice material, allowing for control of the various parameters under which stain reduction is carried out.

This section summarises various poultice materials tested, presenting ways in which they can be used, treatments they may be suitable for, and their limitations. Every case is different, and these will vary with each treatment. Table 3 presents recommendations for each type of poultice material discussed, including product information and application tips.

The class of materials based on cellulose includes paper pulp, cellulose powder, wet-strength tissue, and cellulose ethers.

Being the polysaccharides that make up primary cell walls of green plants, cellulose is extremely hydrophilic, and its products readily absorb aqueous solutions. Its ease of use and inertness make it an extremely useful poulticing material.

Paper pulp and cellulose powder poultices generally maintain good contact with the substrate through complete drying. As with any poultice application for stain reduction, allowing the poultice to dry completely is essential to ensure the stain is pulled into the poultice; if the poultice is removed before evaporation is complete, a concentrated amount of stain can redeposit on or just below the ceramic surface, often becoming more visible and disfiguring. Wet-strength tissue, while the easiest poultice to apply, does not always maintain contact as it dries. While cellulose ethers are a viable option, other gels have been found to be more effective as poultice materials.

One such gel is made from agarose. Like cellulose, agarose is a linear polysaccharide from plants, specifically species of Asian seaweed. It is soluble only in hot water ($T > 85^{\circ}\text{C}$) and gels upon cooling to a semi-flexible film within a few hours. Studies show that little to no residues are left behind, even without a barrier tissue (Warda and others 2007).

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Material	Product Information	Application Technique	Pros	Cons
Paper pulp	<ul style="list-style-type: none"> • Acid-free, ash-free pulps (Filter Flockenmasse, formerly supplied by Mike Schafers at Custom Machine and Design) • DEAE (diethylaminoethyl) paper pulp (Sigma-Aldrich) 	<ul style="list-style-type: none"> • Mix into damp slurry with chosen solution. Allow complete drying before removal. • Can make own pulp by blending paper sheets in blender with deionized water and letting dry. 	<ul style="list-style-type: none"> • Conforms to smooth and uneven surfaces. Easy to apply and remove when dry. • DEAE paper pulp ideal for rinsing phase. 	<ul style="list-style-type: none"> • If not shredded fine, tends to clump and may result in uneven stain reduction. • Danger in applying slurry too wet and causing tidelines.
Cellulose powder	<ul style="list-style-type: none"> • Alpha cellulose (Sigma-Aldrich, Whatman) 	<ul style="list-style-type: none"> • Mix into damp slurry with chosen solution. Allow complete drying before removal. 	<ul style="list-style-type: none"> • Conforms to smooth and uneven surfaces. Easy to remove when dry (brushes off). 	<ul style="list-style-type: none"> • More difficult to apply than paper pulp due to finer particle size. Not very absorbent, meaning that repeated application may be necessary.
Wet-strength tissue	<ul style="list-style-type: none"> • Kaydry EX-L (Kimberly-Clark) 	<ul style="list-style-type: none"> • Dampen sheets with chosen solution and lay on (smooth) surfaces. Allow complete drying before removal. 	<ul style="list-style-type: none"> • Easy to apply, with fast drying time allows for speedy results. • Ideal for application where limited moisture is desired or for follow-up rinsing. 	<ul style="list-style-type: none"> • Often does not maintain contact throughout drying, especially on concave surfaces.
Agarose gel	<ul style="list-style-type: none"> • Agarose powder (Universal Medical) 	<ul style="list-style-type: none"> • Make gel of desired concentration and mix with chosen solution. Functions at pH 4.5-10. Can mix with paper pulp for added adsorption. Cast in thin sheets or blocks and cut gel to desired shape to lay onto ceramic. Allow complete drying, or remove after short time to replace with adsorbent material such as Kaydry. 	<ul style="list-style-type: none"> • Easy to make and apply. • Easy to remove with no residues left behind. • Can control degree of penetration. • Use with water, chelator, solvent, or bleach. 	<ul style="list-style-type: none"> • Need gravity to keep gel in contact with substrate. • Not highly adsorbent so requires addition of paper pulp to hold stain in poultice on drying.
Laponite gel	<ul style="list-style-type: none"> • Laponite® RD (conservation suppliers) 	<ul style="list-style-type: none"> • Make into thick gel with warm water and chosen solution. Applied over (recommended) barrier of gampi usuyo paper and allowed to dry completely. 	<ul style="list-style-type: none"> • Affinity for ceramic surface creates good adhesion and strong pulling power of poultice. • Ideal for pulling stains out of cracks. 	<ul style="list-style-type: none"> • If allowed to dry directly on surface, hard film is tenacious to remove. Residues left behind may alter surface of ceramic.

Table 3. *Poultice materials: product information and application tips.*

Agarose gel can be made with chelating solutions, oxidising bleaches, or organic solvents, and is easy to make: a gel made with de-ionised water alone can be placed into a solution of chosen reagent and, within a few hours, the gel will equilibrate with the solution.

Perhaps the most useful quality of an agarose gel poultice for ceramic-stain reduction is the ability to control its pore size and thus its permeation into a ceramic body. When a heated agarose gel cools, the randomly-coiled polymer chains become double helices, creating a three-dimensional network with even pores. Varying the gel concentration (possible range between 0.5 and 5%) determines the pore size. Lower concentrations have larger pores (hypertonic with the ceramic), yielding greater penetration and permeability

into a ceramic. Conversely, higher concentrations yield a lesser-penetrating poultice. Practically speaking, agarose gels can be adequately used for a variety of stains, depending on how the gel is constructed.

Clay-based gels are another poultice option. The authors use Laponite RD, a synthetic silicate clay, but other options include Sepiolite (hydrated trisilicate) and Attapulgitte (hydrated magnesium–aluminium silicate). All have associated health risks, and many have been found to leave residues behind or present difficulty during removal if allowed to completely dry on porous surfaces, such as ceramic and stone (Lee and others 1997; Vergès-Belmin and Siedel 2005; Warda and others 2007).

Category of Stain	Characteristics	Approach suggested
The more straightforward ones	<ul style="list-style-type: none"> Stain is mostly near surface, readily accessible through loss or crazing/cracks in glaze No sensitive components adjacent to stained area Often the case for porcelain and higher-fired bodies 	<ul style="list-style-type: none"> Use poulticing material that allows ample access of reagent to the stain e.g. paper pulp, cellulose powder, 1-2 % agarose gel Follow standard approach, using chelator, then bleach; rinse superficially afterwards with deionized water and with material that has a strong affinity for the reagent used, e.g. DEAE paper for citrate ions
The ones on rather delicate ceramics	<ul style="list-style-type: none"> Access to stain is made more difficult with vulnerable/sensitive adjacent components Often the case for ceramics with unstable enamels (particularly early ones) and gilding For ceramics that have either a wood, ivory, metal component 	<ul style="list-style-type: none"> Use poulticing material that allows for careful control of the amount of reagent to the stain e.g. KayDry tissue, 3-5% agarose gels, Laponite RD Test carefully first whether water alone or low concentration bleach; use chelators only if no contact with sensitive components can be guaranteed Only superficially rinse afterwards
The extensive, deeper ones	<ul style="list-style-type: none"> Stain has permeated throughout the body and is abundant Stain is localized, but intense, related for instance to a specific loss or crack in an otherwise non-crazed glaze Often the case for earthenwares that have been extensively used 	<ul style="list-style-type: none"> Determine goal of treatment as to whether a surface application could achieve the desired aesthetic improvement or whether entire stain must be reduced Ideally a <u>surface application</u> of the reagent (chelator and bleach respectively) is desired, using a poulticing material that will carefully control the amount in contact with the ceramic e.g. agarose gel If <u>entire stain needs to be reduced</u>, use poulticing material that allows for abundant application of reagent e.g. paper pulp, along with relatively high concentration of reagent (chelator and bleach respectively). Apply poultice slightly beyond area of stain to counteract formation of tidelines. Rinse carefully afterwards so as not to bring to surface remaining staining materials
The stubborn ones	<ul style="list-style-type: none"> Stain is resistant to standard chelators/bleach Often the case for ceramics that have been exposed to the elements, and the stain has become “weathered” through exposure to the outdoors, burial, or particularly harsh previous treatments Stain has been set, possibly “cooked” in place through usage Stain is compounded by oily or greasy component For archaeological ceramics or those associated with cooking 	<ul style="list-style-type: none"> Use chelators, testing at different pHs, e.g. citrates, EDTA or careful application of acids (wet surface pre-treatment if acids used) or still solvents that are also weak chelators, e.g. acetylacetone Use poulticing material that allows for careful control of the amount of reagent to the stain e.g. Kaydry tissue, gels, or with strong ability to retain staining material e.g. clays, agarose gels/cellulose powder mix Remain aware that approach may need to be modified after initial application of reagent, as stain is broken down and now more mobile and readily absorbed by poultice

Table 4. General classification of different types of stain on ceramics and approach suggested for their reduction.

If used with a barrier tissue, Laponite gels can be effective at strongly pulling stains from a body, especially those held within cracks, without presenting challenges in the removal of the dried poultice.

Case Studies

Although it is not possible to present all the ceramics treated as part of this multi-year study, four general categories emerged that capture the range of problems one may encounter. Table 4 outlines each group, as well as the suggested approach for stain reduction. Presented below is one case study from each category, demonstrating the protocol in

action. One important point is that our knowledge of stain-reduction principles keeps evolving, and, in some cases, our approach would be slightly modified if faced with the same problem. Furthermore, these tests relate exclusively to objects in the Winterthur Museum collection, which holds mostly European, American, and Chinese export ceramics from the 17th to the 19th centuries.

The first category represents a standard approach with a straightforward stain on a mochaware tea bowl with a stable ceramic body void of any sensitive components (table 5). After a bleach poultice, the interior remained stained and patchy, and this reaffirmed the need to begin with a chelator to address ionic interactions holding the stain. Subsequent chelator–bleach poultices successfully reduced the stain.

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The second category characterises cases where a particular component of the ceramic may be affected during stain reduction, for instance a creamware teapot with a historic pewter repair (table 6). The goal was to reduce the stain on the exterior, while preserving evidence of use on the interior and not affecting the pewter. The approach consisted of applying first a protection to the sensitive component, then targeting the stain with appropriate poulticing materials and oxidising bleach, allowing for application at the surface and locally. The third category presents a suggested approach for porous ceramics with deeply-penetrating stains overall due to specific glaze losses. A pearlware pitcher with staining that penetrated through an interior glaze loss demonstrates this (table 7). The protocol of chelator–bleach–rinse was carried

out successfully, the goal being to reduce staining on the exterior surface only, using a low-porosity agarose gel. The fourth category, illustrated by a slipware dish, represents those cases where stains prove particularly stubborn. Tests with chelators and bleaches showed how the stain could be reduced, but irregularly, creating areas that appeared overcleaned. The approach consisted first in using agarose gel, with acetylacetone to break down greasy residues, and bulked with cellulose powder to absorb them. After a few applications, the procedure for stain reduction returned to a standard approach, applying a low-porosity agarose gel with a chelator, followed by an agarose gel rinse with water/denatured alcohol (table 8).

Mochaware tea bowl and saucer (Staffordshire, late 18th century, Acc. #2008.0053.002.1a,b, H4.2cm D10.7cm)

- Staining clearly associated with use; extensive overall in tea bowl obscuring pale earthenware body and giving impression glaze is tinted yellow

Before treatment:



Treatment

1. Oxidizing bleach in paper pulp poultice (15% H₂O₂, pH 8.5 with NH₄OH) applied only on interior, with incandescent lamp to aid in heating and polyethylene sheeting to control evaporation
2. Chelator in paper pulp poultice (5% ammonium citrate, pH 8.5 with NH₄OH)
3. Repeat step #1

After treatment:



Rationale

- For total stain reduction to take place, the chelator needed to be applied first; this could have been a two-step treatment only
- Sodium citrate would have been just as effective as chelator, without posing risk of acidic residues

During treatment: after first bleach poultice showing still-stained interior



Table 5. Case Study #1: straightforward stain reduction treatment (Photos: Winterthur Museum).

Creamware teapot with enamel decoration and historical pewter repair (Staffordshire, 1770, Acc. # L2007.1031.1a,b, H13cm W19.1cm)

- Staining overall, yet particularly accentuated in crazed glaze, at losses and along crack; clearly associated with use (tea)
- Treatment aims to improve overall appearance, yet leaving stains within the interior, and not affecting historical pewter repair at spout

Before stain reduction:



Treatment

1. Pewter collar protected with microcrystalline wax and Parafilm® M
2. Bleach in Kaydry tissue poultice (first 10%, then 15% hydrogen peroxide made to pH 8.5 with NH_4OH) to reduce overall stain
3. Localized bleaching of crack in Laponite RD poultices (20% carbamide peroxide at pH 8.2), applied with and then without barrier tissue
4. Deionized water/denatured alcohol rinse in Kaydry tissue poultice

After treatment:



Rationale

- Use of chelator not desired because of metallic component; two applications of low-penetrating bleach ideal for reducing staining just at surface
- Effect of bleach accentuated by covering poultice with polyethylene film and under warm incandescent light for a few hours before air drying
- Use poultice with stronger pulling power, e.g. Laponite RD, only where necessary

During treatment: dry Kaydry tissue poultice prior to removal; as it dries, it conforms and stays in better contact with convex surfaces



Table 6. Case Study #2: stain reduction on a delicate ceramic (Photos: Wintertbur Museum).

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Pearlware pitcher with enamel and lustre decoration (Staffordshire, mid-19th century, Acc. # 1959.1354, H 17.4 cm, W 21.9 cm)

Before treatment:

- Heavy brown staining – heaviest throughout interior, but also evident on exterior and in concentrated patches around design elements
- Stain entered through glaze crazing and area of exposed body on bottom interior of pitcher
- Inorganic components of stain, likely migrated from hard water that was carried in this vessel



Treatment

After treatment:

1. Chelator in agarose gel poultice (4.5% agarose saturated with 2.5% sodium citrate, pH 8.5 with NH_4OH) applied in thin strips on undecorated areas the exterior. After 10 minutes to 1 hour, stain visibly broke down, and gel strips were replaced with squares of Kaydry tissue dampened with citrate solution to adsorb remaining materials
2. Bleach in Kaydry tissue poultice (20% carbamide peroxide, pH 8.5 with NH_4OH) to remove remaining stain
3. Deionized water rinse in Kaydry tissue poultice for final rinse



Lessons learned

During treatment: strips of agarose-citrate poultice visibly breaking down stain, replaced with squares of Kaydry tissue at edges

- Multiple applications of low-penetrating, low percentage of chelator were ideal for reducing staining just at surface
- If agarose gel poultice was left to dry on surface, not all staining material was pulled into it and stain deposited at the surface, just under the glaze; replacing gel with Kaydry tissue after a period of time served to avoid this problem



Table 7. Case Study #3: stain reduction of an extensive, deep stain (Photos: Winterthur Museum).

Earthenware (slipware) dish with colored slips and lead glaze (Samuel Malkin, Burslem, Staffordshire, 1726, Acc. # 2010.0004.001, D 35.1 cm)

Before treatment:

- Localized, irregular stains that masked the cream color of the slip, reducing the contrast between the background and the most important decorative elements (also composed of slightly raised brown/orange slips)
- Tests showed how application of low concentration chelator or bleach tended to specifically clean some areas, while leaving the darker stains unaffected; likely because stain includes greasy or oily components, possibly cooked into place (related to use)



Treatment

1. Initial overall cleaning in zeolite/enzymatic bath to ensure even penetration of aqueous reagents and to reduce risk of pushing deeply ingrained dirt into ceramic body
2. Agarose gel chosen as it allows careful control of solvent (in this case acetylacetone, also a mild chelator, within a water phase); poultice left an hour under polyethylene film, then allowed to air-dry; four applications made
3. After fourth application, tidelines formed indicating how stain had now broken down; further testing determined that 2% agarose gel with sodium citrate, followed by rinsing with agarose gel in 80/20 deionized water/denatured alcohol now could evenly reduce stains without causing tidelines

During treatment: after surface cleaning and two applications of Agarose/cellulose powder gel blocks in 20% acetyl acetone



Rationale

- With stubborn stains, be ready to adapt approach and choice of materials as treatment progresses, since early phases of treatment may disrupt stain, allowing it later on to be effected by materials to which it was impervious at first
- Use of solvents in an aqueous phase can be effective when aqueous reagents fail, both in terms of chelating stain and rinsing residues
- Note that this treatment is still underway at time of publication; overall brighter appearance of buff-colored background already contrasts better with the decoration, but improvement still desired by curator

During treatment: with the agarose gel blocks still wet on the surface; these can be cut to exactly match the area where the stain is present, serving also to minimize the impact of the reagent on other component of the ceramic



Table 8. Case Study #4: reduction of a stubborn stain (Photos: Winterthur Museum).

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Conclusion

Where do we go from here? It is hoped that many conservators will consider the proposed sequence of steps for stain reduction on ceramics and begin to test it, using the methods and materials presented here. It is clear that each stained ceramic requires careful consideration and its own treatment protocol, based on localised testing and observations. This approach allows for a logical and controlled selection of materials and methods, offering a good likelihood for a successful outcome, while minimising the risks for unwanted results.

Our main goal now is to have conservators try the techniques, materials, and sequence proposed, and later contribute their observations to the conservation community. This could be through tests done with a specific chelator, bleach, or poulticing material, or related to a specific kind of ceramic body. To this effect, we have thus far presented two day-long advanced seminars to select groups of conservators at the Metropolitan Museum of Art (May 2012) and the Walters Art Museum in Baltimore (January 2013). The participants are provided a series of chelators in agarose gel blocks with which they can safely conduct tests on a broad range of ceramics, and they are encouraged to share their results with us and the conservation community. Similar to the changes in approach that occurred following Richard Wolbers' work on the gel cleaning of decorative surfaces (Wolbers 2000), we believe stain reduction on ceramics can be achieved safely and successfully with a strong understanding of the properties of ceramic bodies, chelators, bleaches, and poulticing materials. This will not be achieved without a few setbacks, and the discovery yet to come of new or modified materials that will work better in specific cases. However, we feel confident in providing an approach that will contribute to the continued advancement of our field. We plan to steadily continue our work, and welcome comments and ideas.

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