

An Overview of Glaze and Glazing Safety

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Overview:

Food safety in functional pottery and chemical safety in the ceramic studio are frequent topics. There are three aspects to this discussion: (1) glaze safety for functional ware in use; (2) the safe handling of chemicals in the studio; and (3) the safe disposal of waste materials generated in the studio. To protect the general population, as well as the environment, three government agencies oversee these three situations: leachability limits for functional ware (FDA), exposure limits for workers (OSHA), and leachability limits for chemical disposal (EPA). Our goal is to provide basic information that should be helpful to navigate these three situations, address some concerns about folklore (as applied to ceramic materials), and propose some testing that may provide a level of comfort for all of us.

General Introduction: “What is the Safe Limit?” versus “Is it There?”

Over the past thirty years, our culture has slowly and subtly changed from an environment of “What is safe?” to “Is it there?”. This change has complicated the discussion of food safety with regards to glaze performance and the discussion of reasonable and safe studio practices. This change has certainly clouded the disposal situation, frequently indefensibly requiring that all glaze waste be treated as hazardous material (with a correspondingly high disposal cost). In addition, confusion about the accessibility of problematic chemistry abounds because not all forms of chemistry can be readily dissolved, either into food (by interaction with the glaze surface) or by the body if ingested through contact. Industrial hygiene texts and treatises tend to add to the confusion because they typically do not distinguish between the chemical form, i.e., metal, oxide, soluble salt, etc., but incorrectly treat all forms of an element as toxic.

General Introduction to Chemistry:

Most of the glaze chemicals commonly used in the studio are inherently safe. By safe, we mean that these materials are either insoluble or have very low solubility in water. A majority of glazes are mostly composed of the oxides of seven elements: silica (Si), alumina (Al), sodium (Na), potassium (K), magnesium (Mg), and calcium (Ca) are of no concern, whatsoever, with regards to solubility. The last, boron (B), is sometimes discussed as toxic, but this is not typically the case for humans (but is for cockroaches). Even if ingested, the solubility in the

body is diminishingly small to zero. The solubility of these seven elements, in elemental form, oxide form, and hydroxide form is listed in Table I.

Table I. Solubility in grams of common glaze elements, oxides, and hydroxides in 100 ml of cold water.¹

Metal	Symbol	Atomic Number	Element	Oxide	Hydroxide
Boron	B	5	i ^a	sl s ^b	NA ^c
Silicon	Si	14	i	i	NA
Aluminum	Al	13	i	i	i
Sodium	Na	11	d (NaOH) ^d	d	42
Potassium	K	19	d (KOH)	vs ^e	107
Magnesium	Mg	12	i	0.00062	0.0009
Calcium	Ca	20	d (Ca(OH) ₂)	0.131	0.185

- a. insoluble.
- b. slightly soluble.
- c. Not Available (This chemical form does not exist.)
- d. decomposes (reaction product).
- e. very soluble.

This does not rule out respirable materials, such as ground quartz (or flint or silica), but straightforward precautions have been developed that reduce or eliminate the threat. Respirable threats are outside of the scope of this paper.²

Chemicals that may be problematic:

The chemicals of concern are the transition metals which provide color to glazes. These are also sometimes referred to as “heavy metals.” These include Vanadium (V), Chromium (Cr), Manganese (Mn), Iron (Fe), Cobalt (Co), Nickel (Ni), Copper (Cu), Selenium (Se), and Cadmium (Cd). Outside of the coloring oxides, there only a handful of others used in glazes: Strontium (Sr), Barium (Ba), Antimony (Sb), Lead (Pb), and Bismuth (Bi). The water solubility of these metals (and oxides and hydroxides) is compiled in Table II.

In recent years, some of the rare earth elements can be added to this list, such as Praseodymium (Pr) and Neodymium (Nd) and, although exceedingly rare today, Uranium (U), which was used in the mid 20th century to create brilliant oranges and greens in lead glazes. We will ignore these for the sake of brevity and because these are exceedingly rare.

¹ All of the solubility data presented in this paper was obtained from: *Handbook of Chemistry and Physics*, 70th Edition, R. C. Weast, and D. R. Lide, editors, CRC Press, Boca Raton, FL, B-67-146 (1989-1990).

² Cigarette smoking can greatly amplify the problems associated with powders, and this should not be overlooked. In the context of smoking, however, all of these discussions essentially become irrelevant: smoking greatly increases the threat and complicates the discussion.

Table II. Solubility of common transition metal colorants in metallic, oxide, and hydrated forms, in grams per 100 ml of cold water.

Metal	Symbol	Atomic Number	Element	Oxide	Hydroxide
Vanadium (V)	V	23	i	0.8	NA
Chrome (III)	Cr	24	i	i	NA
Manganese (II)	Mn	25	d	i	0.0002
Manganese (IV)	Mn	25	d	i	NA
Iron (II)	Fe	26	i	i	0.00015
Iron (III)	Fe	26	i	i	NA
Cobalt (II)	Co	27	i	i	0.00032
Nickel (II)	Ni	28	i	i	0.013
Copper (I)	Cu	29	i	i	NA
Copper (II)	Cu	29	i	i	i
Selenium (IV)	Se	34	i	38.4	NA
Cadmium (II)	Cd	48	i	i	0.00026
Strontium	Sr	38	i	0.69	0.41
Barium	Ba	56	d	3.48	5.6
Lead	Pb	82	i	0.0017	0.0155
Bismuth (III)	Bi	83	i	i	0.00014

Of these elements only five are regulated by a federal agency and their permissible limits are listed in Table III. Testing for these elements is conducted using a TCLP test (Toxicity Characteristic Leaching Procedure). It is important to recognize that to be leachable and thus to be considered hazardous, the element must be soluble in water. In the oxide form, these elements are usually have limited solubility in water.

Table III. U.S. EPA allowable limits in ground water for heavy metals in parts per million (ppm) or milligrams/liter. Elements of interest in glaze are highlighted.

Heavy Metal	U.S. EPA Allowable Limits (ppm or mg/liter)
Arsenic (As)	5.0
Barium (Ba)	100.0
Cadmium (Cd)	1.0
Chromium (Cr)	5.0
Lead (Pb)	5.0
Mercury (Hg)	0.2
Selenium (Se)	1.0
Silver (Ag)	5.0

The issues of Pb and Cd are well documented and monitored by the FDA for glaze safety (as well as for ground water by the EPA). Since almost all ceramic artists now avoid using Pb, we can ignore the Pb issue for this discussion. Cd is of concern, but it now almost always added as

an inclusion pigment – a form that is both insoluble in water and in a typical glaze. The pigment is encapsulated in zircon to prevent its dissolution and to provide stability of Cd-Se based reds in glazes regardless of firing atmosphere.

The issue of heavy metals is pertinent to all three aspects of ceramic ware: making, disposal, and use. So what about safe handling these in the studio? What makes a material basically safe and what is should be avoided? If these are in the glaze, should we be concerned? (Generally not.) The key to understanding what chemistry can be a problem is rooted in the chemical form of these materials. With few exceptions, the oxide forms are insoluble in water – this is important.

Chemistry and Chemical Forms of Problematic Materials:

Elements occur in many different forms and the nature of that form dictates its level of solubility and thus its potential toxicity. We can group chemistry into three general forms: (1) limited solubility (elemental forms, oxides, etc.), (2) high solubility (salts), and (3) vapor forms (highly soluble in the body).

Chemical forms with limited solubility:

Elements that are bonded with oxygen (oxides) typically have very low solubility and occur in two forms: crystalline or amorphous (glassy). In addition, as a general rule, chemistry that is bound up in a glossy glaze is the least potentially toxic form – glasses tend to have limited solubility in water meaning that the chemistry is simply not available to wreak havoc. Crystalline forms tend to have higher solubility and for this reason it is common to prefer a glossy glaze to a matte glaze for functional ware. It appears to be the more complex structure of a glass (the silicate network) that reduces the solubility of elemental species.

For a glass, chemical durability increases with increasing glaze firing or melting temperature. Fluxes weaken the glass structure (and as a consequence reduce the melting point of the glass or glaze). Therefore, lower melting point glasses tend to have greater solubility in water, i.e., lower chemical durability. As a general rule, functional ware glazes should be formulated to be fired to at least Cone 1.³

For colorants in particular, and this case, transition metals, stains provide a very highly stable option. Stains are typically either based on zircon (ZrO_2-SiO_2) or a spinel-type structure ($RO \cdot R_2O_3$ like the mineral Spinel: $MgO \cdot Al_2O_3$). In almost all cases, these two structures are essentially insoluble in water and almost completely insoluble in the glaze. These stains are a

³ Firing a low temperature glaze to a higher temperature does not solve the problem. The increased flux level necessary to reduce the melting temperature cannot be rectified by increasing the firing temperature. This is a glaze composition/formulation problem.

ceramic analog to pigments in house paint. The particles retain their integrity in the glaze and provide color by virtue of the particle size.⁴

Chemical forms with potentially high solubility (problematic):

Salts tend to be soluble in water and that solubility is part of the definition of a salt. Salts are composed of a cation (a positively charged metal ion) and an anion (a negatively charged ion). Table salt, NaCl, is the most common salt. (Copper sulfate, copper nitrate, copper chloride are all salts of copper and thus are termed copper salts.) For a material to be toxic, the cation has to be accessible to the body. Cations in solution can be readily absorbed by the blood stream and human tissue, making these forms particularly dangerous.

The solubility of salts is often orders of magnitude greater than the solubility of the elemental, oxide, or hydroxide form. For example the solubility of Co(OH)₂ is 0.00032 g/100 cc, but the solubility of CoCl₂ is 426 grams/100 cc of water – a factor of 140,000! The use of salts in the studio represent the greatest potential chemical safety issue for the modern artist. Table IV lists the solubility of the transition metal salts that are of interest as glaze colorants.

Table IV. Solubility of transition metal salts colorants and other common oxides found in glazes.

Metal	Symbol	Atomic Number	Carbonate	Chloride	Nitrate	Sulfate
Vanadium (V)	V	23	NA	NA	NA	unknown
Chrome (III)	Cr	24	NA	i	s	i/s
Manganese (II)	Mn	25	0.0065	72.3	426.4	52
Iron (II)	Fe	26	0.0067	64.4	83.5	sl s
Iron (III)	Fe	26	NA	74.4	150	sl s
Cobalt (II)	Co	27	i	45	133.8	36.2
Nickel (II)	Ni	28	0.0093	64.2	238.5	29.3
Copper (I)	Cu	29	i	0.0062	NA	d
Copper (II)	Cu	29	i	70.6	243.7	14.3
Cadmium (II)	Cd	48	i	140	109	75.5
Strontium	Sr	38	0.0011	53.8	70.9	0.0113
Barium	Ba	56	0.0022	37.5	8.7	0.000222
Lead	Pb	82	0.00011	0.99	37.65	0.00425

⁴ The contribution of the stain particle size is evident to anyone who has ball milled a glaze too much. The color response of the pigment, and thus the color of the glaze, tends to wash out with longer milling time due to a reduction in the pigment or stain particle size.

Chemical vapor forms (very dangerous):

The most dangerous form of any element is in the vapor form, typically a result of a high temperature process where the element is hot enough to volatilize as a gaseous elemental species. This situation would be observed in metals smelting such as the environment associated with steel making. Next to gaseous forms ionic salts pose the greatest danger.

For the artist, this is not a threat. If a metallic species were to volatilize in the kiln, the vapor, although highly reactive, is not stable. Once the vapor encounters a cold surface, the vapor condenses (and usually reacts to form an oxide), at a relatively high temperature. In other words, the vapor will condense on the piece, the refractory, or in the kiln stack (exhaust). This is a very different situation than that observed by the metal smelting industry. Unfortunately, however, this is where most of the toxicity data was originally generated – from metal workers.

This discussion likely raises the question of salt or soda firing – and we will use the two interchangeably for this discussion. Salt firing relies on the volatilization of the sodium to then condense on the ware during the firing (or potentially during cooling). It has been argued that vapor is potentially dangerous. First, Na does not vaporize below about 900°C (about Cone 010) and will therefore condense, usually in the smokestack or on the refractory (or ware) during the firing and or cooling cycle. The anionic species forms a gas that does exit the kiln, either as chlorine gas (Cl₂) or as CO₂. Either way, venting the space is usually sufficient to prevent any safety issues. Regardless, Na in the vapor form is not a safety concern (although it does attack the kiln furniture and refractory) and proper ventilation takes care of the Cl issue.

Functional Glaze Safety and the FDA:

The Food and Drug Administration (FDA) and other similar government organizations around the world have established safety limits for several elements that are typically industry specific. For example the pharmaceutical industry has list of 15 elements that are monitored, while the ceramic industry has only two: Lead (Pb) and Cadmium (Cd). It is not a question of if these are present but if they can be leached from the glaze surface, i.e., if they are soluble in water (usually with vinegar or acetic acid). They can be present in the glaze provided they are not leachable – their solubility (leachability) limit must be below a specific concentration value. Also, as the testing methods improve, this solubility limit decreases.

For most artists, the major FDA problem, Pb, has been essentially eliminated from studio practice for decades. It is rare to have a potter that has Pb in a glaze intended for functional ware. Industrially, Pb is still used in glazes because it is the closest thing to “magic” in ceramics. Pb greatly increases the glaze durability and lifetime in service for commercial dinnerware.

Also, commercial manufactures have to meet the FDA Pb leachability test, as well as the limits for Cd release. The same is true for imported ware.

Getting Functional Ware Tested for Leachability:

First, if you do not have Pb or Cd in your glaze, it is unlikely that your glaze needs to be tested.

Barium may be the only issue for concern. It may be prudent to have glazes that are high in Barium tested, but these glazes are not very common for functional ware. To be safe, plan that the ware will be able to pass the EPA test for Ba in ground water (100 ppm), but recognize there are no FDA established limits for Ba leachability from glazed ware. If the glaze is glossy and the firing temperature above Cone 1, the need for testing is greatly reduced. Just having Ba in a glaze does not constitute a problem. Also, if you have glazes that contain Ba, you may be able to reduce the Ba level without adversely affecting the gloss quality or color response because a small amount of Ba goes a long way.⁵

It is becoming more common to substitute strontium (Sr) for Ba, but there is even less information from the FDA on Sr and the EPA does not monitor nor test for Sr. Again having a gloss glaze fired at a sufficiently high temperature greatly limits the leachability and thus any potential toxicity issues.

While you may wish to have a glaze containing Cu tested for Cu leachability it is probably unnecessary. You likely pick up more copper from your plumbing than you obtain from the glaze in normal use. In addition, if you wash the ware prior to first use, in simple soap and water, any soluble Cu will be eliminated. The reason that the Cu level decreases after washing (once) is that Cu tends to volatilize in the kiln during firing (i.e., form a vapor) and condenses on the ware in the cooling cycle. We tested a Cu glaze years ago and found just this: the first test found measurable Cu levels in the water but the second test measured a drop by a factor of four. To put this in perspective the first test found 200 ppb (parts per billion)⁶ versus 50 ppb Cu for the second test – this is a factor of 2000 lower than the Ba detection limit by the EPA.

Finally, to substantially eliminate any threats, and to provide piece of mind, always wash the ware prior to use in soap and water *the first time*. You may consider adding a note with your pottery that recommends this practice in general, even if you do not have a glaze with metal oxide colorants. Because of vaporization and condensation, it is possible to collect chemistry

⁵ Testing several years ago demonstrated that substituting 0.05 BaO for CaO, on a Unity Molecular Formula (UMF) basis produced an excellent gloss. Higher BaO levels did not improve the gloss quality.

⁶ Parts per billion (ppb) is 1000 times less than parts per million (ppm), i.e., 1000 ppb = 1 ppm.

from prior firings on the surface of your ware – washing with soap and water prior to use is prudent.

Studio Safety with Respect to Coloring Oxides:

The best approach for glaze safety is to select raw materials that are either insoluble or have limited solubility in water. This approach essentially eliminates salts (and with good reason). It may also create a preference for using frits where possible. For example, a commercial dinnerware manufacturer that uses Pb in their glaze, adopted a Pb-based frit 30 years ago to minimize handling issues and potential toxicity for their workers (and to avoid OSHA issues).

Transition metal oxides are generally insoluble in water, as demonstrated in Table II. These oxides can dissolve into the glass (glaze), provided they are not, as mentioned previously, incorporated into a spinel or zircon structure. Even if the colorants are added to the glaze as an oxide (or as a salt), once the glaze melts these metals become insoluble trapped in the glass matrix. The same rules of a glossy glaze fired at or above Cone 1 apply.

The use of salts however, can also be misleading. The price of transition metals is likely linked to the amount of metal available. For example, the oxide form may be the least expensive because when heated, all of the metal oxide remains. This also means that less metal oxide would be needed compared to the level of oxide obtained from a metal salt on firing to keep the color response similar. Table V lists the yields of metal salts, compared to the oxide, for the transition metals of interest. In some cases the metal yield is remarkably small (certainly for the nitrates). The highest yields (outside of the raw oxide) are typically with carbonates. This means that you need to use more of the salt to obtain the same color compared to an equivalent amount of oxide.

If you do use a soluble salt to obtain a coloring metal oxide, be aware that the glaze waste likely contains a soluble form of that metal. This means that disposal should be done properly. This also means that decanting a glaze suspension after leaving the glaze to settle in a bucket is not a recommended practice. Soluble materials will be in the decanted water. This is true even without metal salt additions – any soluble species remains in the water. If you are planning to re-hydrate or re-suspend the glaze in the future, allow the glaze to dry out so the soluble species remain in the glaze. Do not filter press, settle and decant, nor slip cast the glaze to remove excess water as this can lead to a significant shift in chemistry. The use of soluble salts raises another issue, evident in Table V, that greater amounts of soluble material would be needed to obtain the same oxide level in a glaze. This creates potential disposal issues with regards to the EPA ground water limits for heavy metals.

Table V. Yield, in grams, of common transition metal salts based on a 10 gram initial addition to a glaze.

Metal	Oxide	Oxide	Carbonate	Chloride	Nitrate	Sulfate
Chrome (III)	Cr ₂ O ₃	10.0		3.2	1.4	2.6
Manganese (II)	MnO	10.0	6.2	2.8	1.4	4.7
Iron (II)	FeO	10.0	6.2	2.8	1.2	4.2
Iron (III)	Fe ₂ O ₃	10.0		3.3	1.5	2.7
Cobalt (II)	CoO	10.0	6.3	2.9	1.3	4.8
Nickel (II)	NiO	10.0	4.0	2.9	1.3	4.8
Copper (I)	Cu ₂ O	10.0	7.6	7.2		6.4
Copper (II)	CuO	10.0	3.6	3.0	1.3	5.0
Cadmium (II)	CdO	10.0	7.5	3.5	2.7	6.2

Folklore?

An example of ceramic glaze (and body) folklore are the reports surrounding the use of manganese (Mn) and its link to Parkinson’s Disease. Mn in a soluble form is a neurotoxin, but this data was generated from the steel industry and the conditions of exposure are dramatically different due to the vaporization of Mn during steel production (and the use of a furnace open to the local environment, that is, without a stack). Inhalation of these vapors creates a readily available reactive species for adverse interactions with the body (and internally through the lungs and mucus membranes). Even small amounts can be readily absorbed into the bloodstream. The oxides of manganese, MnO and MnO₂, are both insoluble in water and do not pose a threat. The Mn is not soluble and therefore not available, cannot be absorbed through the skin or even an open cut, and even if ingested, cannot dissolve into the blood stream. Mn obtained from a salt (chloride, nitrate, or sulfate) is soluble, so if the source of Mn is a salt, exercise appropriate care.

Studio Safety with Respect to Disposal:

Issues related to the disposal of glaze waste should only be concerned with the potential for heavy metal dissolution. If metals in the glaze dissolve and enter the ground water, there are several potential problems, not the least of which is the EPA. Not all metals are monitored, as identified in Table III, but we can treat them all as if they were. The situation can be safely addressed in basically two ways: (1) use colorants that are insoluble (stains, oxides, etc., but not salts) when possible; (2) treat the waste to ensure there is no solubility in water. Ideally, if both

stains and soluble salts are used in the studio, keep the waste streams separate to facilitate disposal.

Solubility of stains and TCLP:

For this discussion, we have assumed, based on my experience, that none of the stains are soluble in water. This idea should be verified, however, and testing is underway with several representative stains, with particular focus on stains containing problematic heavy metals (V, Cr, Co, Cd, Se, etc.). To determine the level of solubility of problematic species, the TCLP test has been established. Essentially, the test involves a liquid:solid ratio of 20:1, i.e., 100 grams of solid waste in 2000 ml of water and the addition of acid to reduce the pH to a level less than or equal to 2.0. (For comparison, vinegar typically has a pH of 3.0.) If the level of the metal is less than 20:1, the testing does not need to be performed. But herein lies the problem: How much Cr is in the stain? This information is not readily available and is generally considered a trade secret by the stain manufacturers. Hence, testing is required.

From another perspective, however, the stain alone has been washed, potentially three times, before packaging and sale. In the form received, the stain should be insoluble in water and any soluble species previously removed by washing. This too needs to be tested for verification.

If we were to assume that a Cr-bearing stain was added to a glaze at a level of 10% and the level of Cr in the stain was at 10%, the overall level of Cr is $0.1 \times 0.1 = 0.01$ grams of Cr per 100 grams of glaze. This amounts to 5 mg/liter – the exact level of the EPA limit for Cr in ground water. If that Cr is not soluble, or if that Cr is only partially soluble, the level of Cr extraction from the glaze waste would fall below the TCLP level for Cr and the glaze would not need to be disposed of as hazardous waste.

Clearly this testing needs to be completed as quickly as possible to demonstrate that our assumption regarding stain solubility (or stability in water) is correct.

Creating an insoluble form for waste – precipitation route:

If soluble salts are used, they would need to be rendered into an insoluble form. Similarly if the stains are demonstrated to have some level of solubility, a second step is in order. One approach, based the solubility levels listed in Table IV would be to add Na_2CO_3 (Soda-ash). The least soluble form of most of the heavy metals is the carbonates. Na_2CO_3 has a relatively high solubility introducing the divalent carbonate anion (CO_3^{2-}) into solution. This will bond with metal cations in solution precipitating the metal carbonate thus creating a lower solubility form. If the problem is Ba the addition of Epsom Salts ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) introduces the divalent sulfate anion (SO_4^{2-}) to precipitate BaSO_4 . While this is a reasonable and informed approach, it may not

be a perfect solution due to unforeseen factors (other precipitating species, the level of additive needed, etc.). If executed with testing this may be an efficient and cost effective solution.

Creating an insoluble form for waste – fusion route:

The other route to eliminating or reducing soluble metal ions is to compact the glaze waste and fire the waste, in a normal kiln cycle, to fuse the material together and tie the metals up in a glassy structure. The same ideas apply in this case as for a glaze: a glossy surface and temperature above Cone 1. If the amount of glaze waste is small, this may be a viable solution. Obviously, if the level is greater, this route can be quite expensive. Also, as stated before, the leachability level of metals from a glass should be tested for verification.

Personal Sensitivity:

What has been discussed previously are general guidelines. This does not address any personal sensitivity issues, which are simply not predictable for the general audience. Personal sensitivity can eradicate the general rules, and in those situations, problematic materials should just be avoided. For example, if you are allergic to fish, don't order fish for dinner.

General Rules for Glaze Safety and Glaze Handling:

1. Glossy glazes fired to at least Cone 1.
2. Avoid, if possible, colorants that are in a water soluble form (salts).
3. Wash the ware prior to first use (or testing) in soap and water.
4. Consider precipitation or fusing as a means of reducing solubility of metals in waste streams. While not fool-proof, this may be an economical approach to safe disposal.