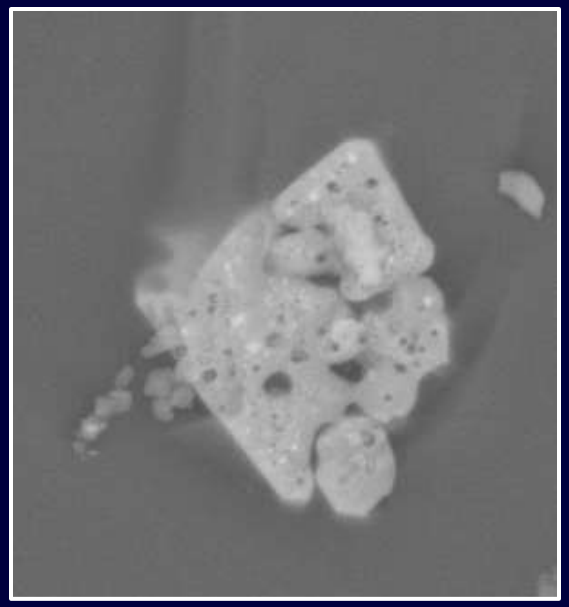
Overview of Glaze and Glazing Safety



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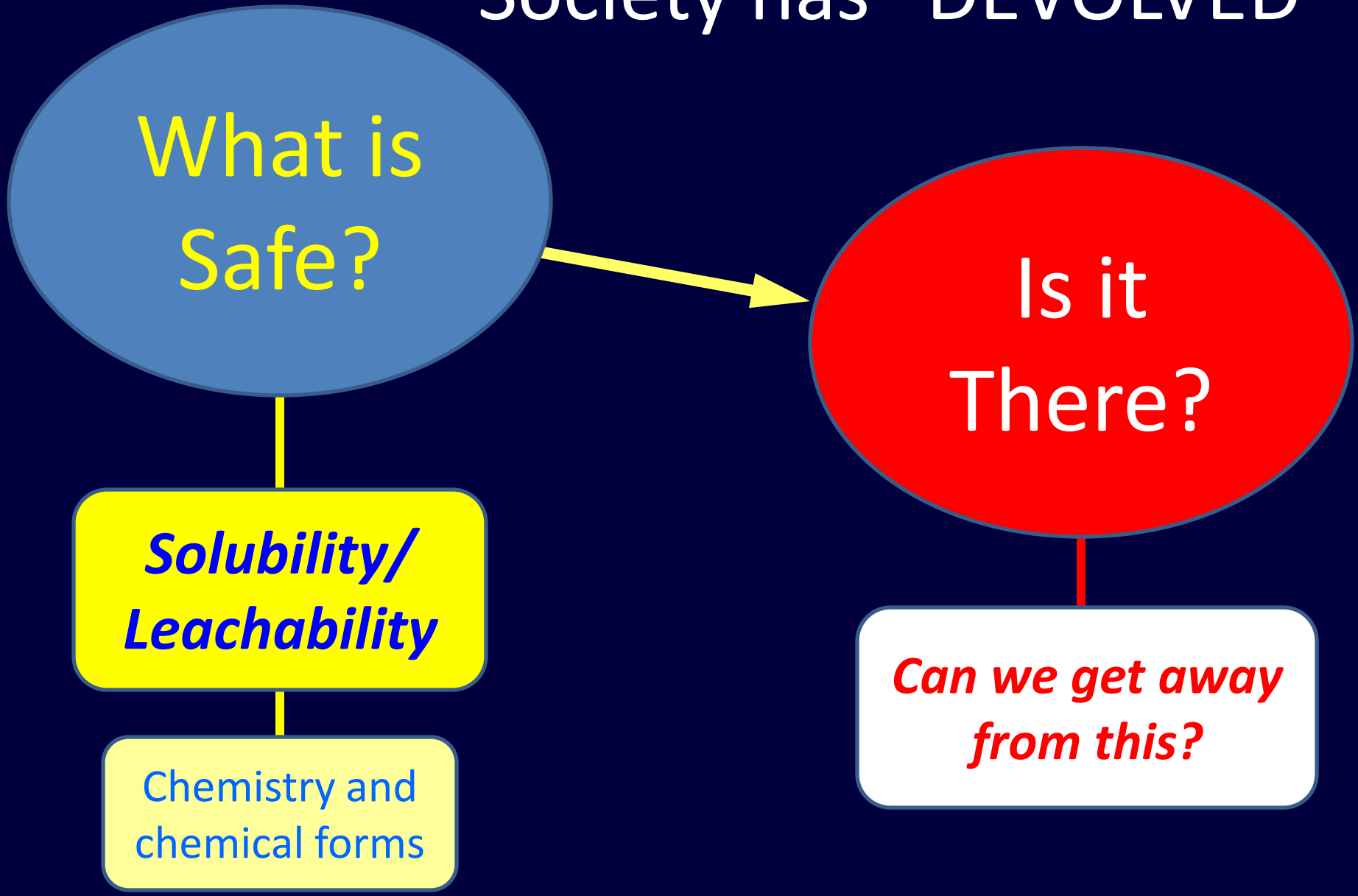
Society has "DEVOLVED"



How should we approach the problem?

Separate into three “groups”.

OSHA, FDA, EPA

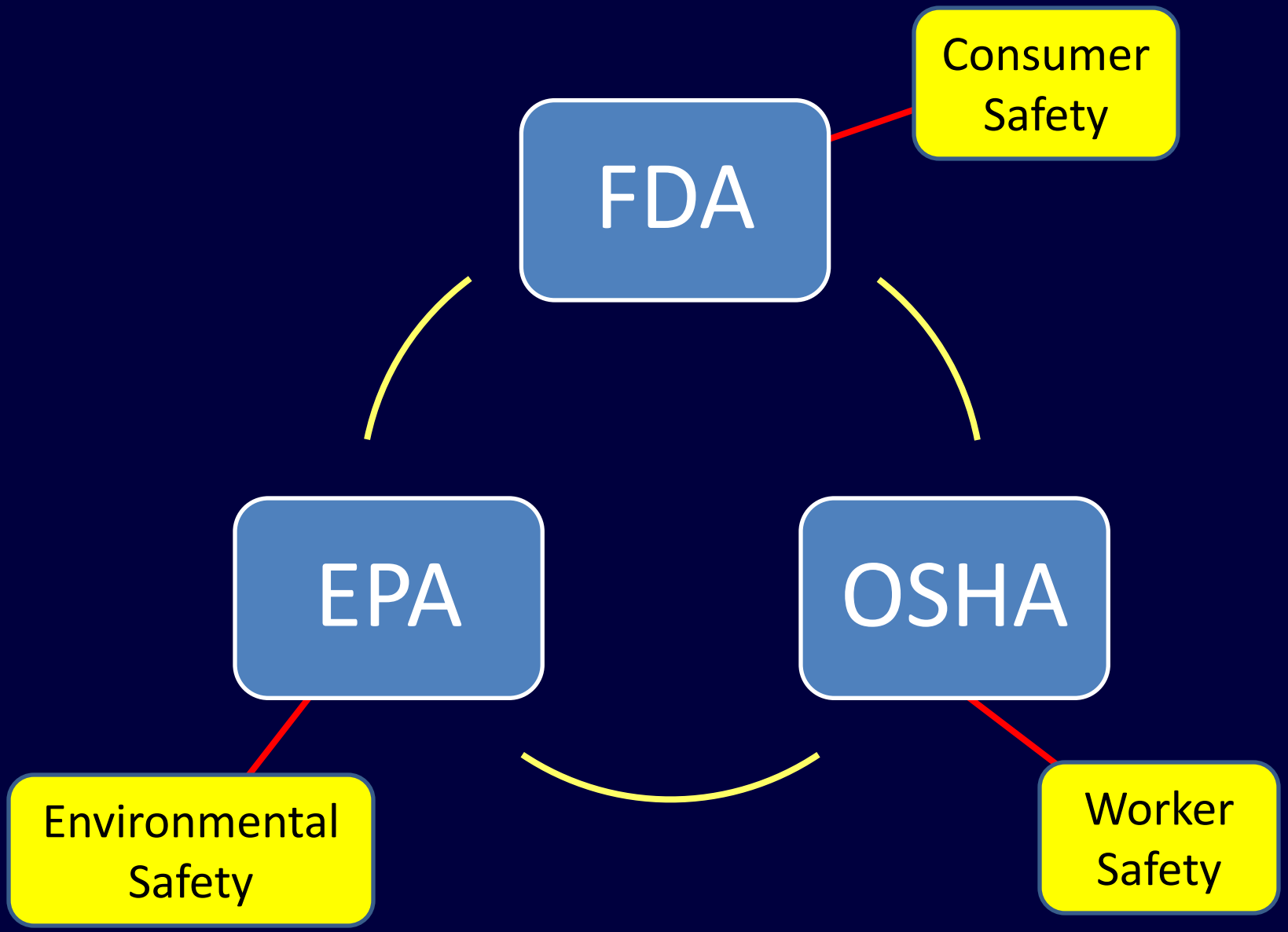
What is Folklore ?

What testing is necessary?

For functional ware?

For peace of mind?

U.S. Federal Government



A Boundary… *(for this talk)*

This is a discussion about chemistry.

We are ignoring Lead (Pb).

This is not a discussion about respirable materials.

No Smoking!

Folklore?

If the a toxic material is present, the glaze must be treated as hazardous.

Elements are dangerous/toxic regardless of their chemical form.

Much of the data was obtained from another industry/situation.

Manganese – a perfect example.

Sodium from salt/soda firings.

Chemistry

Basic oxides in most glazes

SiO_2

Al_2O_3

B_2O_3

Na_2O

K_2O

MgO

CaO

These are basically insoluble in water

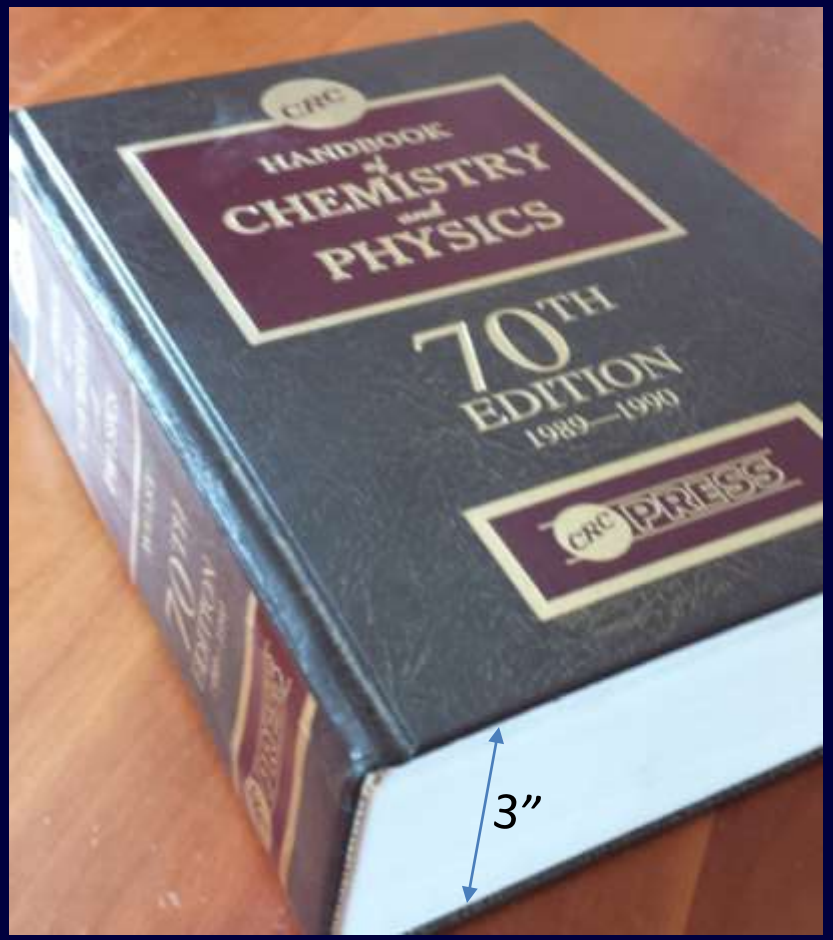
These are also not toxic

Solubility / Leachability?

This is all about solubility in water.

If not soluble in water, there is no safety issue

All of the information is readily available.



What is the issue?

Metals

Metals give color.

In the oxide, form, in glazes, typically not an issue.

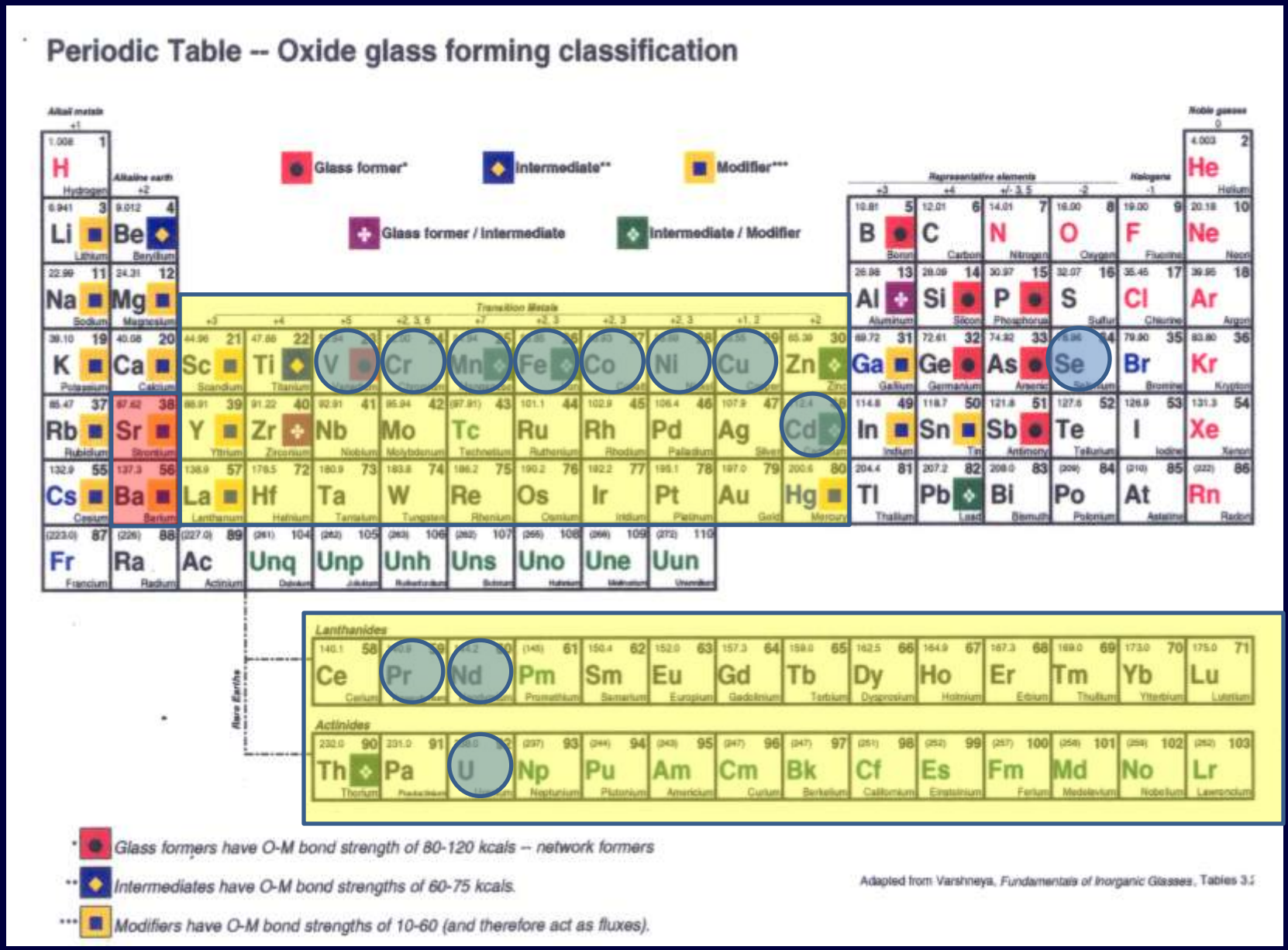
Only a few forms are problematic.

V, Cr, Mn, Fe, Co, Ni, Cu, Cd, U, Pr, Nd

Outside of the metals, there are only a few problematic elements:

Sr, Ba, Pb

The Periodic Table of Elements



What is Important? What may be toxic?

"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

Chemical Forms at Issue

Metallic or elemental form.

Oxide form.

Salt form(s).

Vapor form.

Chemistry comes in different forms.

Metallic or elemental form. **Co** (Cobalt)

Rare form for most metals ***Low solubility in water.***

Oxide form. **CoO**

Common form. ***Very low solubility in water.***

Form in glazes and glasses.

Salt form(s). **$Co(NO_3)_2$**

Uncommon form. ***Often soluble in water.***

Tend to be unstable and decompose.

Vapor form. **$Co_{(v)}$**

Rare form. ***Most dangerous form.***

Common in the smelting industry.

Solubility of Metallic, Oxide, & Hydroxide Forms

Metal	*Symbol*	*Element (Metal)*	*Oxide*	*Hydroxide*
Vanadium (V)	V^{5+}	i	0.8	NA
Chrome (III)	Cr^{3+}	i	i	NA
Manganese (II)	Mn^{2+}	d	i	0.0002
Manganese (IV)	Mn^{4+}	d	i	NA
Iron (II)	Fe^{2+}	i	i	0.00015
Iron (III)	Fe^{3+}	i	i	NA
Cobalt (II)	Co^{2+}	i	i	0.00032
Nickel (II)	Ni^{2+}	i	i	0.013
Copper (I)	Cu^{+}	i	i	NA
Copper (II)	Cu^{2+}	i	i	i
Selenium (IV)	Se^{4+}	i	38.4	NA
Cadmium (II)	Cd^{2+}	i	i	0.00026
Strontium	Sr^{2+}	i	0.69	0.41
Barium	Ba^{2+}	d	3.48	5.6

Solubility: (grams / 100 ml of water)

Implications for Glaze Safety?

Most coloring metals are insoluble in the oxide form.

This is likely also true with stains.
(more later on stains)

If the metal is bound-up in the glass phase, or in a crystal (as in a stain), then it is typically insoluble.

Metal Oxides are not generally a problem for the ceramic industry.

Chemical Forms at Issue

Metallic or elemental form.

Oxide form.

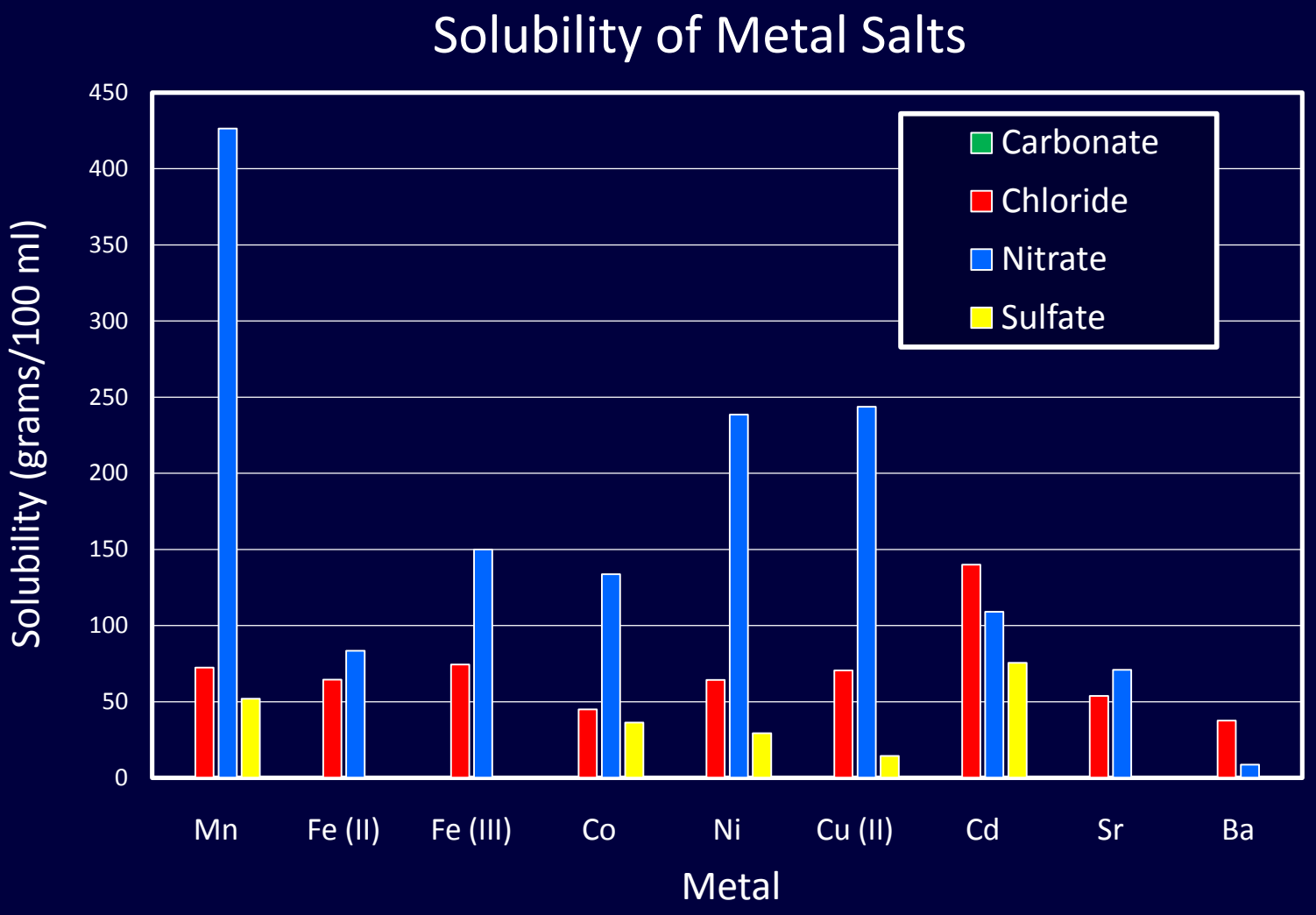
Salt form(s).

Vapor form.

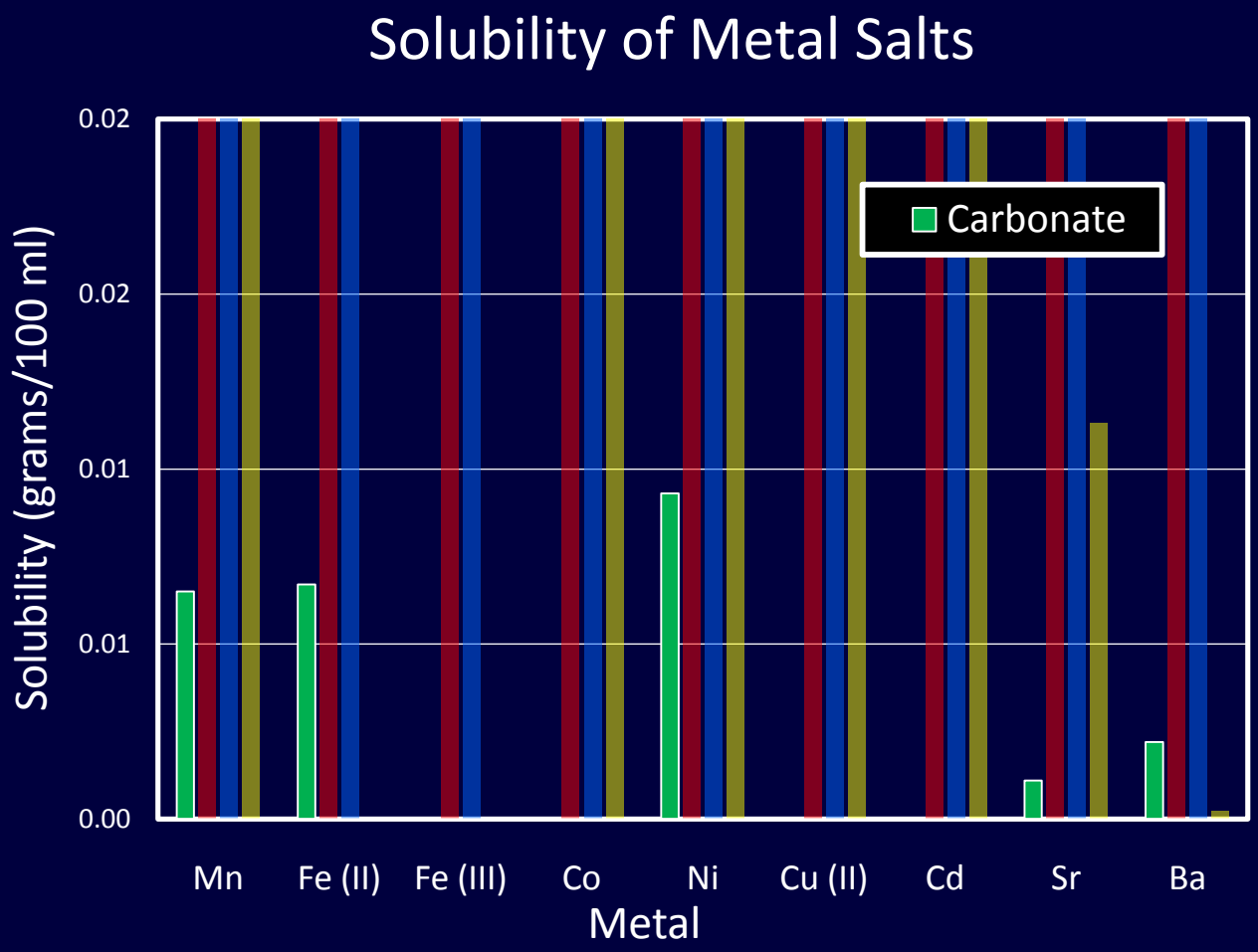
Solubility of Metal Salts

Symbol	Carbonate	Chloride	Nitrate	Sulfate
V^{5+}	NA	NA	NA	unknown
Cr^{3+}	NA	i	s	i/s
Mn^{2+}	0.0065	72.3	426.4	52
Fe^{2+}	0.0067	64.4	83.5	sl s
Fe^{3+}	NA	74.4	150	sl s
Co^{2+}	i	45	133.8	36.2
Ni^{2+}	0.0093	64.2	238.5	29.3
Cu^{+}	i	0.0062	NA	d
Cu^{2+}	i	70.6	243.7	14.3
Cd^{2+}	i	140	109	75.5
Sr^{2+}	0.0011	53.8	70.9	0.0113
Ba^{2+}	0.0022	37.5	8.7	0.00022

Salt solubility comparisons



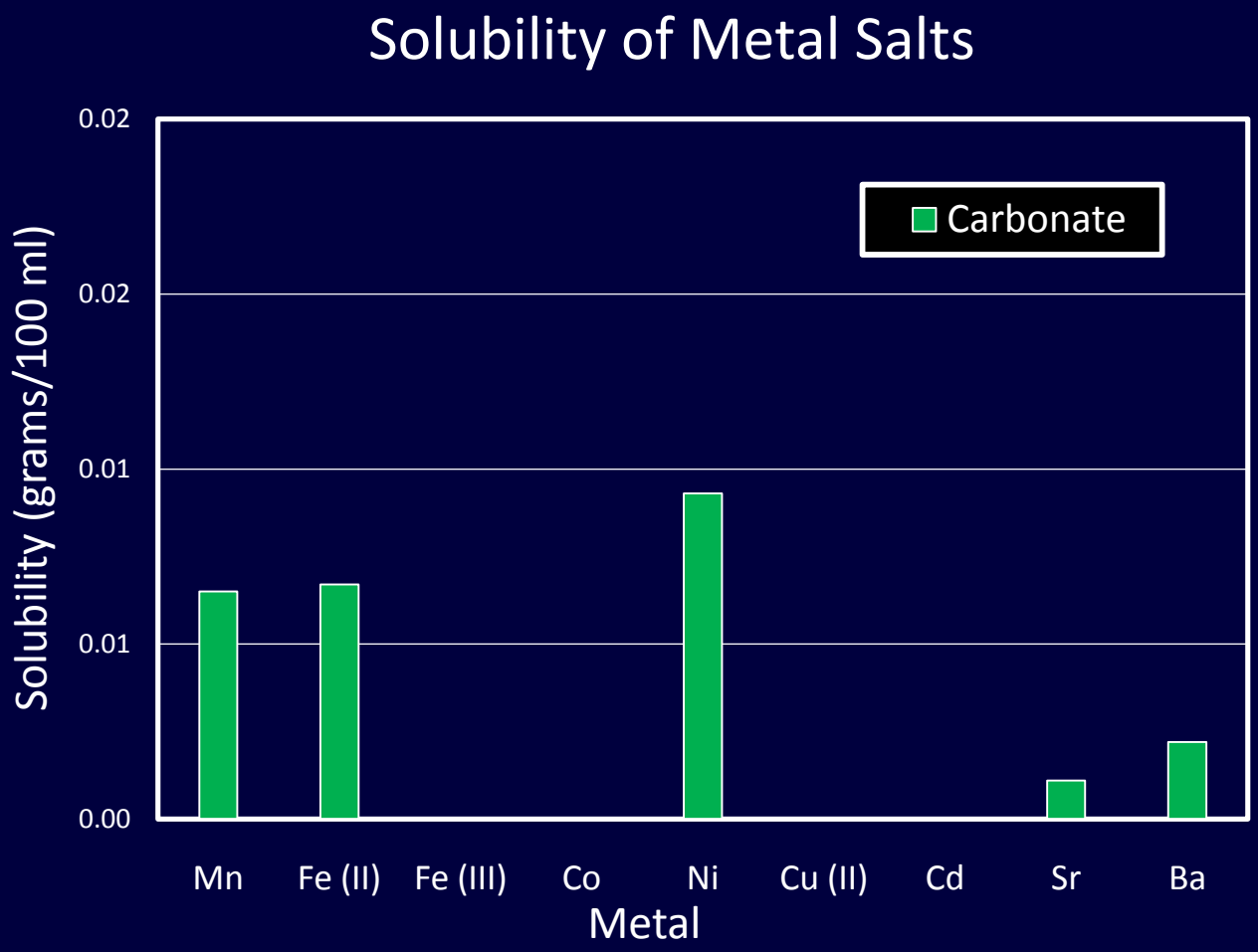
Carbonates are the least soluble



An Opportunity to address waste?

(Before we label it "waste".)

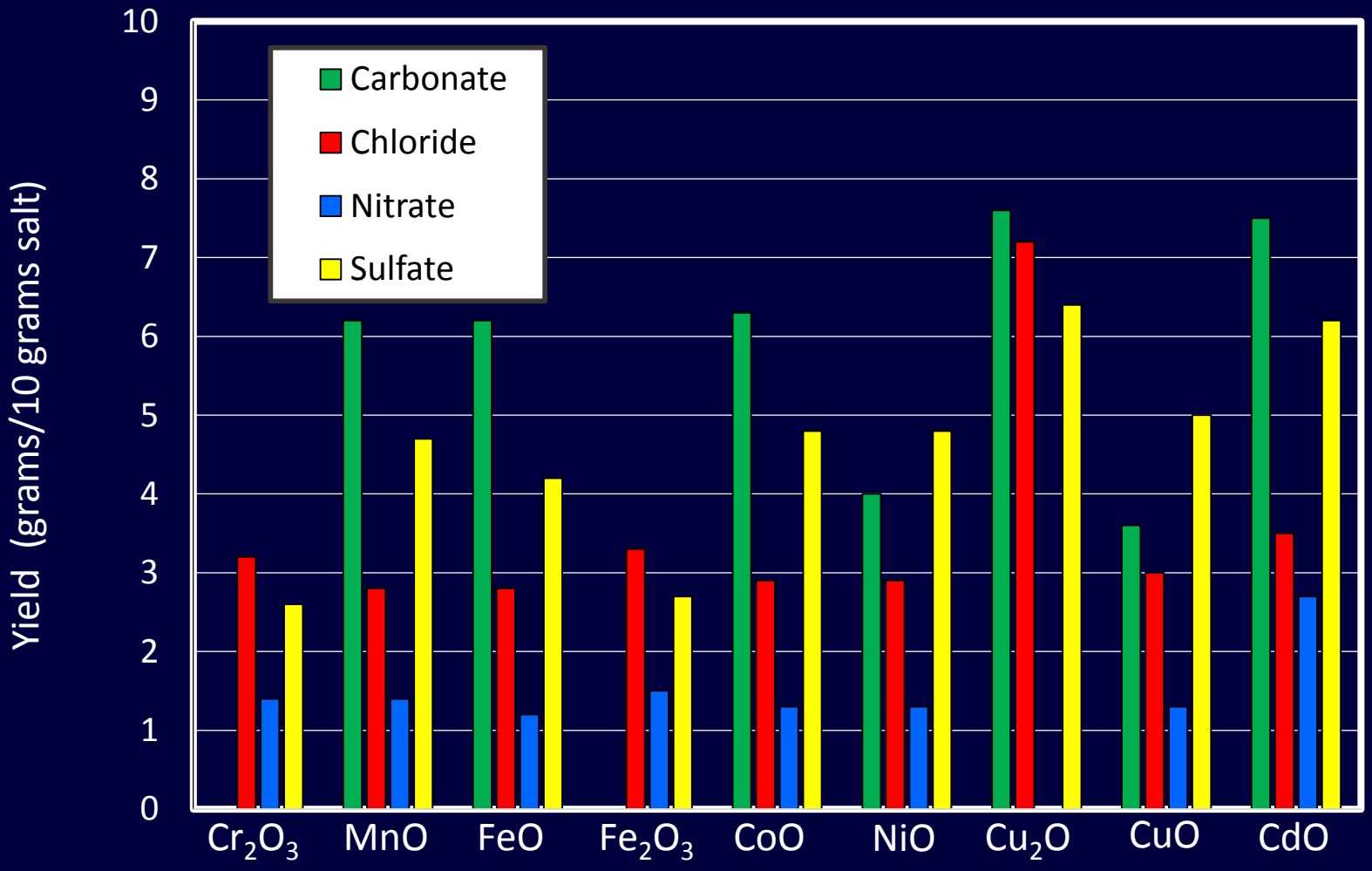
Carbonates are the least soluble



An Opportunity to address waste?

(Before we label it "waste".)

Metal Oxide Yields from Metal Salts



Chemical Forms at Issue

Metallic or elemental form.

Oxide form.

Salt form(s).

Vapor form.

The Vapor form of Chemistry

This is the most dangerous form.

Rarely, if ever, observed in ceramics outside of the kiln.

Unfortunately, this is where most of our toxicity data has been generated – due to the steel and metal smelting industries.

Industrial Hygiene texts do not typically differentiate the form of the chemistry. This is a problem.

Chemistry in a Vapor form is rarely a problem for the ceramic industry.

Vapor in the kiln condenses on the ware

(or in the exhaust stack)

Salt and soda firing (obviously?).

Lead (Pb) and Copper (Cu) tend to vaporize and then condense. (But we are ignoring Pb.)

Copper condenses on the ware.

Copper is not regulated, nor should be considered toxic.

i.e., there are no published exposure limits.

Copper testing will be addressed later.

Safety in the Studio

Metal ions in solution (dissolved metals) are a problem.

In this form, the metals have the greatest potential for health issues.

Use chemistry forms that are most stable:

Oxides

Carbonates

Stains (zircon, spinel, or inclusion)

One issue with soluble metals

(and all soluble materials in the glaze)

- Most glazing is applied to green or bisque ware (not to dense, fully vitrified ware).
- This is convenient, but recognize that the porosity helps glaze application.
- The glazing process is essentially a slip casting type operation and the water enters the ware.
- Dissolved ions then move into the body with the water from the glaze. This can substantially change the chemistry of the glaze as applied.

The other issue with soluble metals
(Yield)

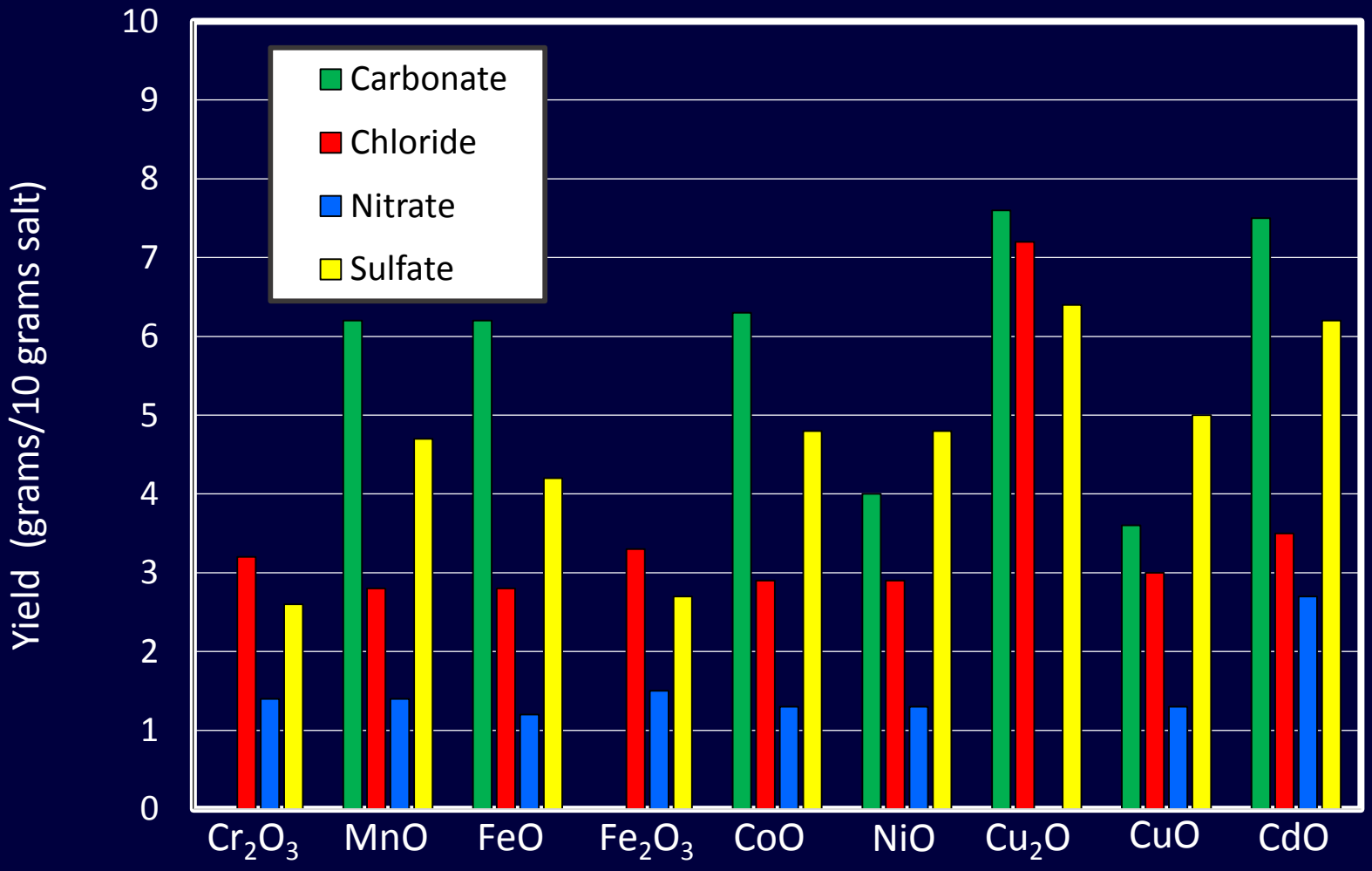
Metal salts provide less metal.

This means that more salt is needed to obtain the same color response compared to using the metal oxide.

Depending on the salt used, the yield may be significantly different. There is no general "rule of thumb" to predict yields.

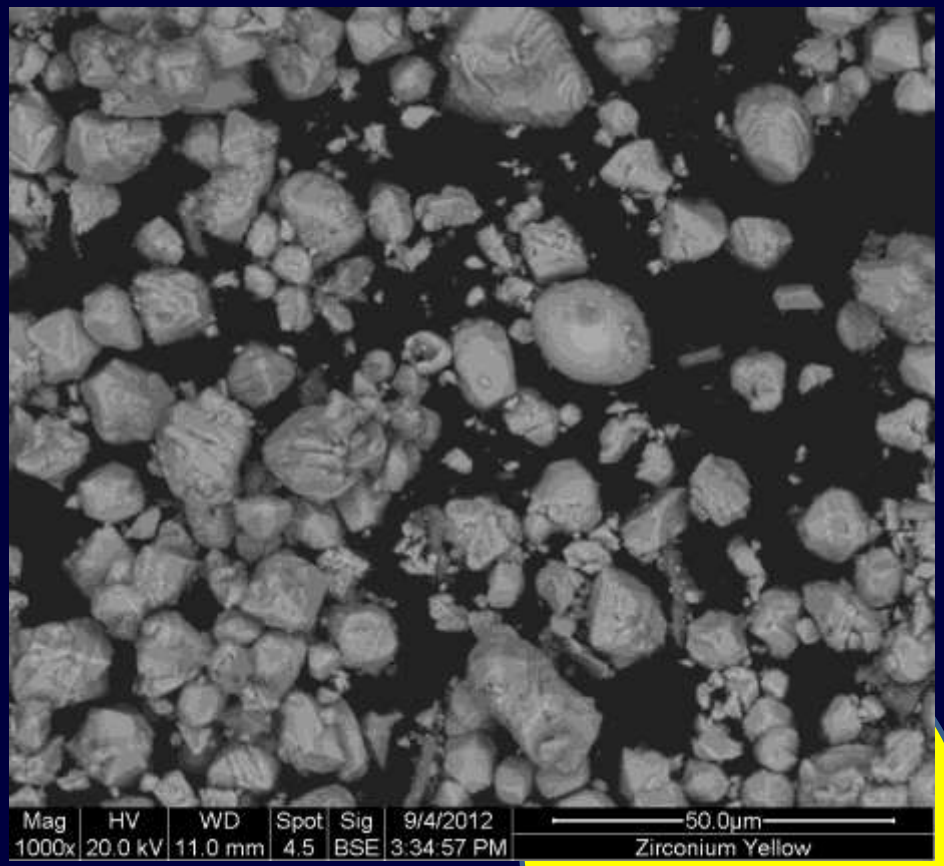
Here is a graphical representation of yields for 10 grams of several metal salts:

Metal Oxide Yields from Metal Salts



Zircon Stains – *a safer alternative*

- Particles tend to be large to provide the color response.
- Zircon is “doped” to provide color.
- For example, vanadium is added to zircon to get yellow (at one level) and blue (at another).
  - Praseodymium can also be used for yellow.

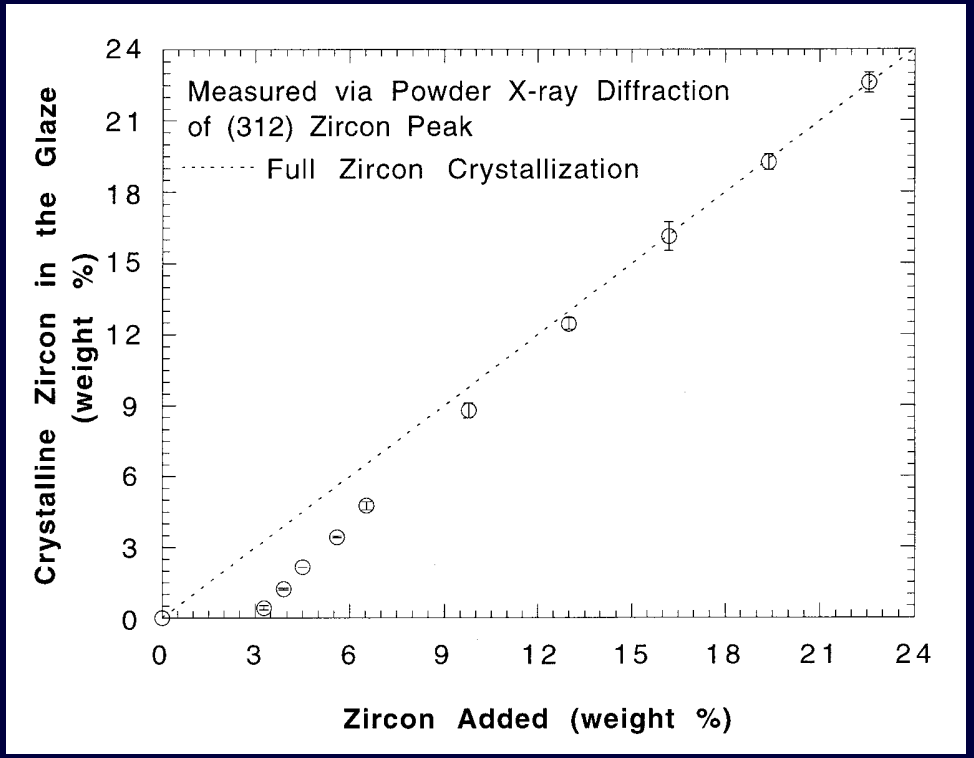


Zircon = Chemistry Stability

Zircon is insoluble in water.

Zircon is only marginally soluble in any glaze.

Therefore, pigments based on zircon (inclusion pigments, stains, etc.) should be entirely safe for functional ware.



The "Other Stain Family": ***Spinel***

Mason Stains, Cerdec/Degussa, etc.

Like zircon, spinels tend to be highly insoluble in glasses/glazes

- Spinel is a family of crystal structures.
- The mineral *Spinel* has the formula $MgO \cdot Al_2O_3$.
- Other common spinels are $FeO \cdot Cr_2O_3$, etc.
- The metal ions are strongly tied up in the spinel structure.

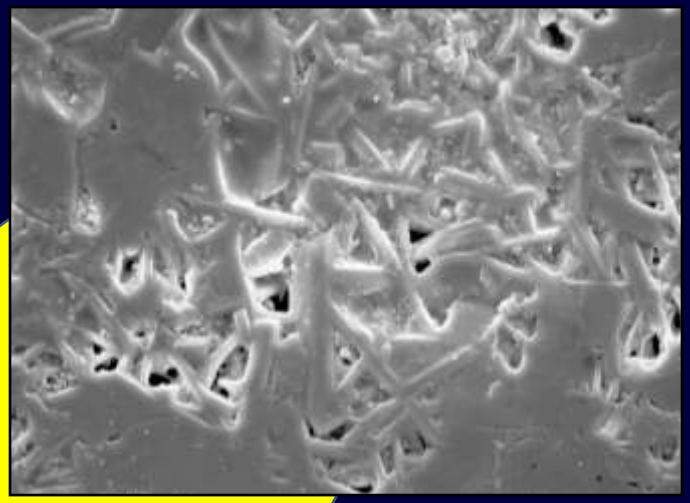
Result: No solubility (in glass or water).

General Guidelines for Functional Ware Safety

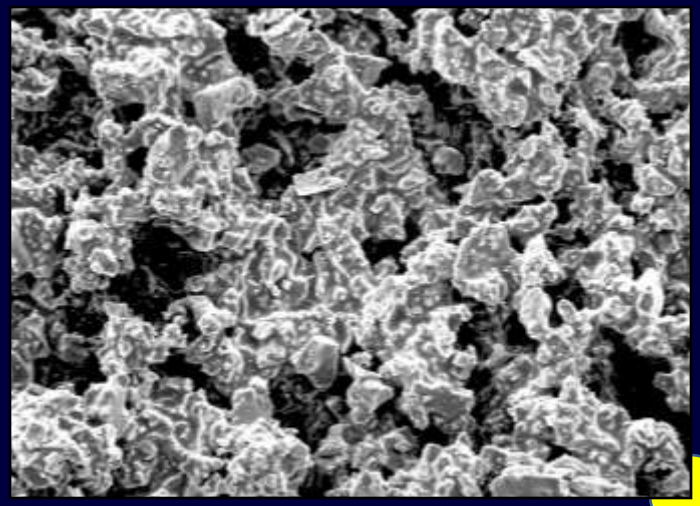
Glaze matures at or above Cone 1.

Glaze should be glossy.

Robust Matte Glaze



Underfired Matte Glaze



Matte Glazes are not chemically durable.

Safety in Use of Functional Ware

FDA Limits for leachability.

What is of concern?

- Lead (Pb)
- Cadmium (Cd)

These are the only two metals that are monitored by the FDA.

What about Copper?

What is the issue with Copper?

Potentially no issues.

Copper is not regulated. There are no published exposure limits.

Copper is not on the EPA list,
nor on the FDA list

(Actually, Cu was the motivation for this talk.)

What about Copper Leachability?

Cu tends to form a vapor during firing.

The Cu vapor condenses on cooling, in the refractory, on the stack, and on the ware.

It forms a thin film on the ware.

If tested, copper appears to be leachable – *in the first test*.

If tested again, the Cu level is greatly reduced. (4x)

How to deal with Copper

(if still of concern)

Wash the ware with soap and water prior to first use or leachability testing.

This should be a standard practice.

Suggestion: wash the ware before sale, or suggest that the ware is washed prior to use.

This is overall a good practice, particularly if you share a kiln – Other species can volatilize in the kiln and condense on the ware – even chemistry from previous firings.

Glaze Safety for Functional Ware

FDA Limits for leachability:

For **Cadmium (Cd)?**

Limit: 0.5 mg/ml

Where does Cd appear?
Inclusion Pigments

Bright reds, oranges, etc.

Pigment particle is encapsulated in zircon

Cadmium-based pigment particles

- Zircon is insoluble.
- Cadmium would normally dissolve into the glass/glaze and would be sensitive to atmosphere
- Encapsulation → Kiln atmosphere independent

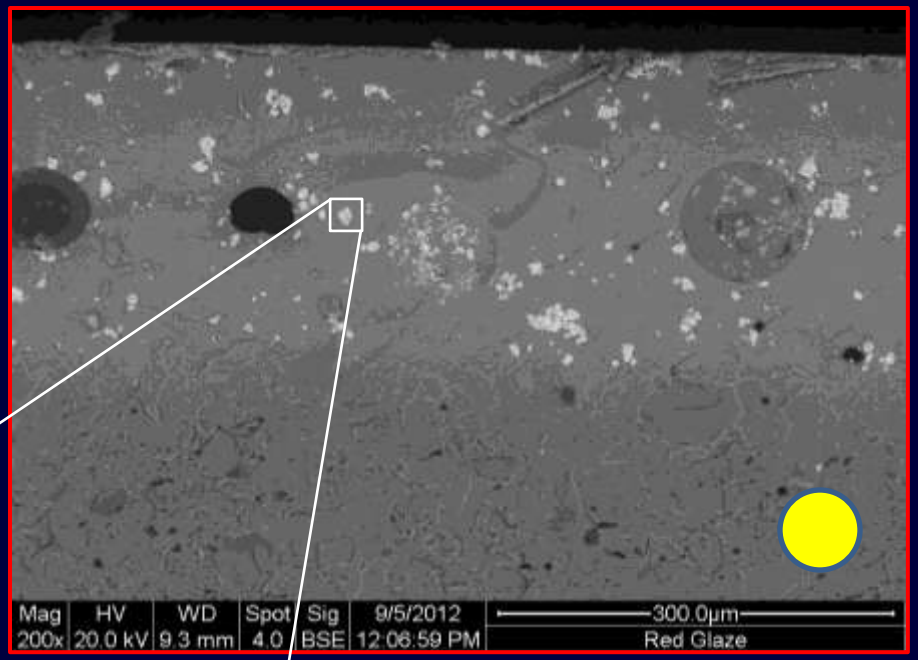
Inclusion Pigments

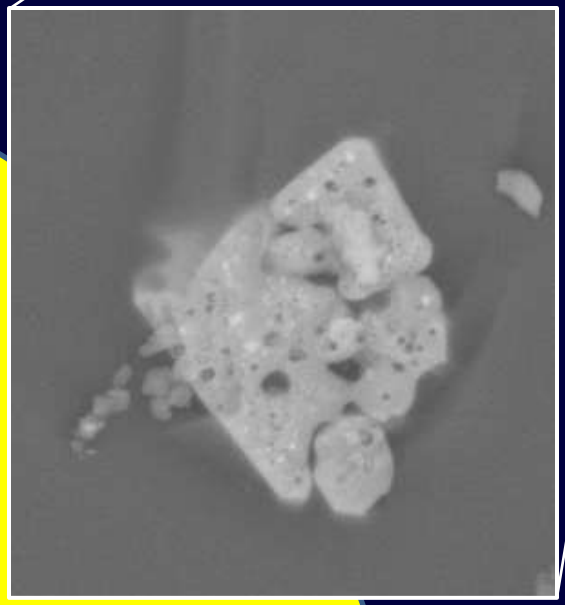
Red

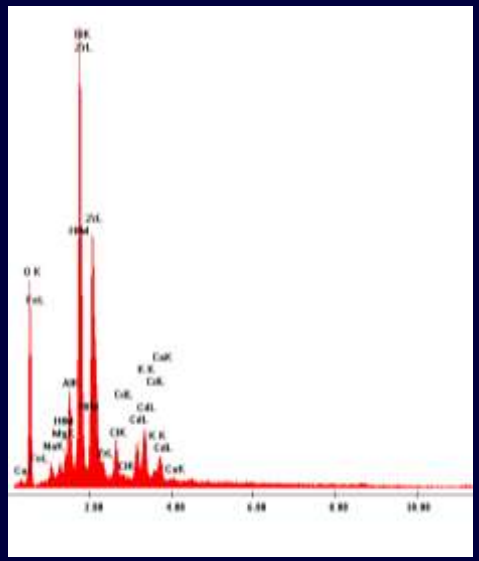
8-10% pigment

Cd encased in zircon

Problem?







Safety in Waste Disposal

Regulated by the EPA.

The standard test is called the TCLP test:

***T**oxicity **C**haracteristic **L**eaching **P**rocedure*

Originally designed for soil testing.

Establishes the allowable limits of several "heavy metals".

Determines the metal solubility under acidic conditions (pH=4)

TCLP Limits for “Heavy Metals”

“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

Does everything need to be tested?

If the level of metal is low enough, NO.

20:1 "Rule"

"*Total Constituent Analysis*"

When the "maximum theoretical concentration of leachate from the waste could not exceed the concentration specified in the toxicity characteristic".

Example – Cr addition

20:1 – liquid:solid ratio.

2000ml water with 100 grams solid.

For example:

Cr-bearing stain at 1.0% in a glaze.

Level of Cr in the stain: 10%

Amount of stain: 1.0 grams.

Amount of Cr via the stain: 0.1 gram.

0.1 gram Cr/100 grams of glaze.

Example – Cr addition (cont.)

0.1 gram Cr/100 grams of glaze.

$\therefore$ 0.1 grams (**100 mg**) in 2000 ml (**2 L**)

This is 50 mg/liter.

The TCLP limit is 5 mg/liter.

If all of the Cr was assumed to be soluble in water (leachable), then the amount of Cr possible would exceed the TCLP limit.

Is this a problem?

The issue is the assumption that all of the Cr is soluble in water.

Even if the Cr was added as a salt, not all of the Cr would be soluble, based on the salt solubility.

In a stain, the Cr is typically not soluble (nor are anything other species).

We need to know (measure?) the leachability of the stains.

What is needed? Next steps?

Testing.

Solubility of stains via TCLP procedure.

- **Both inclusion stains and zircon/spinel stains.**
- **Involve the stain manufacturers.**

Evaluate for the three problematic metals:

Cr, Cd, Se

Test glazes/glaze waste for Ba/Sr leachability:

- **Follow the test for Pb.**
- **Use data to establish practical limits.**

Personal Sensitivity

This is outside of anything discussed.

Problematic materials should simply be avoided.

This is not predictable nor regulated.

General Rules for Safety

Food Safety:

Glossy glazes maturing above Cone 1.
Wash ware prior to use.
If you insist on testing, wash ware prior to testing.

Studio Safety:

Avoid colorants that are in a water soluble form (metal salts).

Environmental Safety:

Consider converting metal-containing materials in a glaze batch to an insoluble form (if necessary).

Thank You

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