The background of the entire page is a photograph of white ceramic dishes, including a large plate, a smaller plate, and a cup, arranged on a purple surface. The text is overlaid on this image.

Lead Glazes for Ceramic Foodware

Richard L. Lehman
Rutgers University

**The
International
Lead
Management
Center**

**A
Primer
for the
Non-Ceramist**

Three blueberries are placed on a small white plate in the bottom right corner of the cover.

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The International Lead Management Center
Research Triangle Park, NC USA

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ABOUT THE AUTHOR

Dr. Richard Lehman is Professor in the Department of Ceramics and Materials Engineering where he conducts basic and applied research in new and traditional forms of glass, ceramics, and polymers. He has particular interest in lead-containing glasses and glazes, glass raw materials and melting reactions, and the chemical durability of glasses and glazes. Dr. Lehman is also active in the field of immiscible polymer blends and is Director of the Center for Advanced Materials via Immiscible Polymer Blends at Rutgers. In addition to research activities, Professor Lehman is active in graduate and undergraduate instruction and he participates in external consulting activities with local, national, and international industries and organizations. Prior to joining the Rutgers faculty in 1982, Dr. Lehman gained eight years experience at Johns-Manville and FMC Corporations where he worked in the fiberglass and industrial chemical fields. Dr. Lehman has over 100 publications and 25 patents on the processing and properties of materials and he is a Fellow of the American Ceramic Society. He received his BS., MS., and Ph.D. degrees from Rutgers University.

ABOUT THE INTERNATIONAL LEAD MANAGEMENT CENTER

The International Lead Management Center was founded in July 1996 and is based in Research Triangle Park, North Carolina, in the United States of America. The Center was established by the international lead industry in response to the need for coordinated international action on the issue of lead risk management.

Although ILMC was founded and is sponsored by the lead-producing industry, liaison and cooperation has been established with the lead products applications sectors. ILMC expertise and advice is therefore available across the full range of issues associated with production, applications, recycling and disposal.

ILMC complements and supports existing international risk management activities and responds to the individual needs of countries who wish to introduce such projects in either industry or their local communities.

The Center welcomes inquiries and requests for either advice or assistance. Requests for assistance are assessed through the Center's considerable network of technical, metallurgical and occupational expertise. ILMC provides assistance by working with national governments and interested parties to identify the most appropriate risk management options.

ILMC activities are supported by an extensive and growing database containing consensus health materials and detailed lead risk information for mining, refining, manufacturing, recycling and associated case studies. The database will also maintain a register of those agencies and organizations able to assist with the funding of community projects.

Lead Glazes For Foodware – An Overview

A stand-alone primer for the non-ceramist

Uses of Lead Glazes in Contact With Food.

Lead glazes can be safely used on a wide variety of ceramic ware, such as earthenware pottery, stoneware, and a range of porcelain type bodies. See Appendix F for a glossary of these and other terms. In fact, the excellent

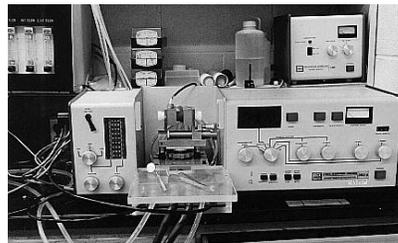


Glazed earthenware bowl, cone 06

properties and wide processing latitude provided by lead oxide [PbO] in the glaze structure make it an ideal glaze component over a wide range of ceramic ware compositions and firing ranges. When properly processed, the lead oxide, which is typically present in concentrations ranging from a few percent up to nearly 50%, is chemically combined in the glass structure and the amounts that can be extracted by food substances or other common acidic media are extremely low, well below established limits set by the FDA, ISO, and other regulatory groups. When isolated instances of high lead release have been measured for ceramic ware, the causes typically fall into one of three categories: [1] the glaze was improperly formulated and did not contain the proper mixture of ceramic oxides as described subsequently in this text, [2] proper firing practices were not followed and the lead oxide was incompletely combined with the silicate glaze matrix, or [3] decorations and/or coloring agents were inappropriately used such that the lead in these agents was easily extracted, or they were applied on inappropriate parts of the ceramic ware.

Measuring Lead Migration from Glazes

Strict international standards exist that limit the amount of lead and cadmium that can be released from ceramic ware in contact with food. Such standards are defined by the International Standards organization [ISO] and are discussed in greater detail in later chapters. Generally, the tendency of lead to migrate from the glaze is greatest under acidic conditions and the standard ISO test defines a 24 h exposure of the ware to 4% acetic acid at room temperature, about 22° C. Such tests must be conducted under controlled laboratory conditions and numerous laboratories are equipped to conduct these procedures. Ware passes this test if the acetic acid contains less than 0.5 – 2 parts per million [mg/l] of lead after the test, depending on the size and shape of the ceramic ware. Flat plates pass if they release less than 0.8 mg/dm² according to the established procedure. Well-manufactured foodware with well-designed lead glazes will easily pass these limits. In addition to the formalized procedures established by ISO, there are other methods for assessing the lead migration potential of foodware, ranging from alternative laboratory methods such as potentiometric electrode methods to much simpler test kits available to the consumer.



Atomic absorption instrument used in measurement of lead release.

The Formulation and Application of Lead Glazes

Historical Development

According to written accounts and from the analysis of archeological artifacts, lead has been used in foodware from ancient Egyptian times to the present. The broad popularity of lead as a glass and glaze constituent stems from the numerous processing and property characteristics it imparts to the glassy state. Among other attributes, lead lowers the melting point of glazes, widens the processing range, imparts surface smoothness and brilliance, and gives the glaze the ability to heal manufacturing defects such as blisters and pinholes during processing.



19th Century Pottery

The main disadvantage of using lead in glazes is the high toxicity of lead when absorbed into the body. This can occur when the glaze is not properly designed and/or is improperly applied to the ware, or poisoning can occur in the factory where lead chemicals are being handling in the glaze preparation process. The historical use of highly soluble lead compounds, such as white lead, exacerbated this hazard. Beginning in the late 1800's, new lead compounds were developed that were much less bio-available and thus reduced the

uptake of lead by pottery workers. Most successful of these approaches was the fritting of lead, a process by which lead oxide is chemically combined in a glassy matrix and crushed to a fine powder. These glassy powders, or frits, keep the lead compounds tightly bonded and have greatly reduced the hazards of working with lead. They are a key element of standard lead glaze practice today.

Ceramic Ware

A wide range of ceramic pottery processes exist today, ranging from the traditional methods of hand fabrication and glazing followed by one or more firings in simple periodic kilns -- much as has been done for centuries -- to modern efficient processes where dinnerware is automatically formed by jiggering machines, fired, glazed and fired again in high speed kilns. In all instances two of the most important variables, as will be repeatedly discussed in later chapters, are the nature of the underlying ceramic body and the temperature to which the ware is fired.

Ceramic body types fall into several categories as indicated in the table:

Ceramic Body	Typical Firing	Description
Earthenware	Low, up to cone 03	Often called pottery, these materials are porous, usually colored or pale white and were originally prepared from natural mixtures of clay and other ceramic materials.
Stoneware	Moderate to High Cone 2 – 10	Dense, impermeable ware, usually colored to pale.
Porcelain	Moderate to High Cone 2 – 10	Dense, white ware, often with high translucency, made from highly refined raw materials.

Raw Materials

The raw materials used for lead-containing glasses in contact with food are principally the same raw materials used for other earthenware, stoneware and porcelain glazes. These materials, mostly beneficiated mineral materials, include clay as a source of SiO_2 and Al_2O_3 , flint [SiO_2], feldspar [$(\text{Na},\text{K})_2\text{O}$, Al_2O_3 , SiO_2], whiting [CaO], dolomite [$(\text{Ca},\text{Mg})\text{O}$], zinc oxide, talc, ulexite/colemanite [B_2O_3] and various frits. Frits are premelted glassy materials that contain certain percentages of important glaze oxides and which are crushed to a fine powder and sold as a commodity to the ceramic industry. Frits are desirable because they enable water-soluble materials to be combined in an insoluble glass matrix. Many alkali and borate oxides are thus rendered more useful as a glaze ingredient by fritting. Lead compounds are also often combined with silica and other ingredients and fritted. The lead in these frits is much less bio-available than the lead in more traditional and more soluble lead oxides and carbonates. Modern practice for manufacturing lead glazed foodware minimizes the use of highly soluble compounds such as white lead and favors the use of more insoluble compounds such as lead oxide or lead silicates.

Safe Lead Glaze Compositions

The formulation and use of lead in glazes in contact with food requires the development of a lead migration resistant composition and a proper firing cycle to permit the glaze raw materials to fuse together into a homogeneous acid resistant glassy surface coating. Although the fundamental design of safe lead glazes is not trivial and requires skill in glass and ceramic formulation technology, some general trends can be identified that will enable the layperson to understand the general approach.

Glazes are glassy substances that are comprised of a silicate network modified with alkalis and other elements to produce the desired properties. Safe lead glazes are resistant to the attack of various food acids, which seek to extract lead and other modifier elements from the silicate network. Generally speaking, safe glazes have a large amount of silica and a low amount of alkali network modifiers. More specifically, oxides can be categorized by their role in the glaze and their general effect on lead release, as indicated below.

Glaze Network Formers	Glaze Stabilizers	Glaze Fluxes
Strongly bind lead	↔ Intermediate	↔ Promotes lead diffusion
SiO ₂	CaO	PbO
ZrO ₂	MgO	Na ₂ O
Al ₂ O ₃	Al ₂ O ₃	K ₂ O
B ₂ O ₃		B ₂ O ₃

[note: Some oxides appear in more than one category and their role depends on the type and amount of other oxides in the glaze]

The formulation of glazes is discussed in terms of the glaze molecular formula and the relative number of moles of the various oxides. One mole of SiO₂, for example, is equal to the number of grams corresponding to the molecular weight of the oxide. SiO₂ has a molecular weight of 60.1, so one mole of SiO₂ equals 60.1 grams. The weight of one mole of other oxides follows accordingly.

One class of foodware safe lead glazes contains low amounts of fluxes such that the moles of the stabilizers and fluxes, as noted above, is approximately 25% of the mole amount of the network formers. Examples of three such glazes, maturing from Cone 06 to 5, are given in the table.

Example Glazes for Foodware Surfaces

[Firing temperatures for corresponding large cone are at 150° C/h heating rate, no soak. Soaking will lower maximum required temperature. Use cones to precisely measure heat work imparted to ware]

Oxide	Cone 5	Cone 1	Cone 06
K ₂ O	1.72%	2.48%	1.52%
Na ₂ O	3.06%	1.63%	1.60%
CaO	7.64%	9.50%	
PbO	16.07%	15.65%	23.10%
CaF ₂			18.33%
Al ₂ O ₃	9.57%	9.57%	6.48%
B ₂ O ₃	6.03%	7.33%	10.70%
SiO ₂	55.90%	53.84%	37.30%
ZrO ₂			0.98%
	100.00%	100.00%	100.00%
Firing Temperature, C.	1196	1154	999
Lead release, base glaze, 24 h, 4% acetic acid, 22° C, mg/l.	0.16	0.02	0.11

Glaze Application Methods

A glaze slip, or water suspension, is prepared from the raw materials selected for use in the glaze. In so-called raw glazes, the individual raw materials [clay, flint, feldspar, whiting, lead oxide] are dispersed directly in water to produce a suspension about the consistency of heavy cream. Fritted glazes usually contain all the necessary oxides precombined in the frit, except for the oxides corresponding to



Applying glaze by the dipping process

a 10% addition of clay or similar suspension agent that is added with the frit to the water. Binders such as sucrose or carboxy methylcellulose are sometimes added to improve the dry strength of the glaze and avoid defects. The glaze can then be applied to the ware in a diverse number of ways, such as the brushing, sponging and dripping methods favored by artists and some potters, to the highly mechanized spraying and waterfall methods used in industry. Hand dipping of ware is a widely used practice [photograph] in large industrial plants and in small potteries. After sufficient drying at ambient or in a heated dryer, the ware is ready for firing.

Firing Method and Temperature Ranges



Pyrometric cones used to measure firing heat work. Slightly slumped free-standing cones at left, Fully down plaque cones at right.

The firing of ceramics is defined and controlled by a seemingly archaic method of temperature measurement that relies on observation of the softening and melting of miniature ceramic cone structures formulated from various ceramic formulations [see photo of partially and fully softened cones in a kiln with fired bowl].

This method, the method of cones, is in reality a highly accurate method for measuring heat work, the product of time and temperature, achieved during the firing process. It is more accurate, reproducible, and subject to fewer errors than many electronic methods based on thermocouples and the like. Cones do, however, have an unusual labeling sequence as illustrated in the table of cones and corresponding temperature values given in Appendix E. Increasing temperature of firing is defined by decreasing cone numbers that begin with a zero (i.e. 010, 09, 08, etc.) until 01 is reached. Subsequent cone numbers commence with cone 1, 2, 3, 4, etc.

Most ceramic dinnerware is firing in the cone 06 [1000° C] to cone 10 [1305° C] range, with earthenware and other porous or highly fluxed compositions occupying the lower part of this range and stoneware and porcelain the upper part.

Firing methods have varied greatly since antiquity and current practice continues to demonstrate a great deal of diversity. The ancient methods consisted principally of wood or coal firing in kilns insulated with refractory stones or simple bricks made of fireclay. Temperatures were usually low and most ware produced was earthenware. These kilns were often located on hills or facing windward directions to promote combustion. The ancient firing methods have gained renewed popularity in modern times among artists and specialty potters. However, the vast majority of commercial ware is produced in highly efficient periodic or continuous kilns fired with gas or electricity. Periodic kilns are filled with ware during a production shift and then fired over a period time ranging from eight to 36 h or more, depending on the size of the load and the type of ware. Continuous kilns fire ware continuously as it is loaded and pushed through the kiln on cars, belts or rollers; the thermal profile of the kiln and the speed at which the ware is pushed through determines the firing time/temperature cycle for the ware. An efficient process developed in recent decades is that of fast firing. In this process, the ware is advanced through a roller hearth kiln in a single layer and at great speeds. The speedy process results in fast heating and cooling, which requires special formulations to avoid the introduction of flaws during the process, and the complete firing cycle can be just an hour to two.

Decorations

Decorations represent an important area of technology in the manufacture of ceramic foodware. From an aesthetic and marketing perspective the use of decorations is critical to the generation of beauty, consumer appeal, and marketplace competitiveness. Principal types of decoration include decals, painted images, direct ink transfer images, and metalization. Decorations can contain lead, cadmium and other toxic materials that require careful application to foodware ceramics in order to avoid consumer ingestion. The three major issues that influence decorated foodware safety are the composition of the decorations, the area of the foodware to which they are affixed, and whether the decoration is underglaze or overglaze.

Decorations are mixtures of pigments and matrix media. The role of the matrix media is to provide a substance into which the pigments can entirely or partially dissolve and/or to provide a bonding agent that adheres the pigments to the ware. The formulation of pigments and the matrix media determines the stability of the decoration with respect to end-use conditions. Although a definite trend exists in the industry to reformulate decorations away from toxic materials, some colors (bright red for example) are difficult to produce without toxic materials [Cd in the instance of red]. Special methods, such as encapsulation, have been developed to address these issues.

When possible, it is desirable to position decorations away from direct food contact areas or other high-risk vicinities, such as the rim of a glass or cup that comes into contact with the consumer. Various regulatory guidelines either prohibit decoration within one centimeter of the drinking rim of such ware or strictly limit the lead release rates from these areas. One method to virtually eliminate consumer exposure to toxic decorations is to put the decoration under the glaze, i.e. to glaze over top of the decoration. This seals the decoration under a layer of glaze and precludes attack from food or dishwasher solutions.



Hand painted decoration

However, a major drawback of this approach is that often-sensitive decorations are required to withstand the harsh high temperature glaze-firing environment in contact with corrosive molten glaze. Special methods exist for fabricating overglaze decorations with durable coatings and fluxes such that they partially dissolve into the glaze when fired to combine the best features of overglaze and underglaze methods. These approaches have collectively become known as inglaze decoration.