PRELIMINARY SURVEY REPORT

The Hall China Company
East Liverpool, Ohio

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INTRODUCTION

Several pottery-making processes involve recognized physical or chemical occupational health hazards. Potential hazards include silica, various metals and chemicals, noise, and heat.

The Engineering Control Technology Branch of NIOSH is conducting a research study to assess and document control methods in the ceramics (clay) industry. Preliminary surveys are conducted to observe the processes and controls in the actual industrial settings and to determine which industrial sites are suitable for in-depth study.

On this preliminary visit, September 29, 1981 we met with Mr. John Sayle, vice president and treasurer, Dr. Robert Beals, research director, (president-elect of the American Ceramic Society) and Mrs. Anna Carnahan, R.N., personnel director and chief nurse. Dr. Beals was our primary host and was most generous with his time and information. We also met with Lester D. McElhaney, eighth vice president of the International Brotherhood of Pottery and Allied Workers, and international representative for the Hall China Company union local. The latter meeting took place at the Unions' international headquarters in East Liverpool, Ohio.

DESCRIPTION AND FACILITIES

The Hall China Company was founded in 1903 in East Liverpool, Ohio. Today, after several relocations and expansions, the company occupies approximately 11-1/2 acres, all under one roof, at the corner of Elizabeth and Ann Streets in East Liverpool, Ohio. All manufacturing is done on the ground floor level of a hi-bay wood and masonry building. There is a basement area under part of the structure. The floors are either concrete or wooden block. The buildings are heated by the waste heat from the kilns. Except for the offices, there is no air conditioning in use during warm weather. This location of the company's operation is labor intensive. There are approximately 500 hourly and 40 salaried employees. Most of them work the day shift. Most of the employees have been with the Company over 10 years.

PROCESS DESCRIPTION

In order to better understand the health hazards and associated control technology, the origin and characteristics of the raw materials in pottery making were discussed. The raw materials breakdown is approximately as follows: 15 to 30% ball clays and koalins; 50% feldspars; and 12 to 18% others. In addition to the body composition there are the glazes which consist of frit, clay, colors, other chemical compounds, and mineral elements.

Since clay is the major raw material, its origin and composition, characteristics, properties, aging, firing, glazing, and overall chemistry were discussed. See Appendix A for details.

The manufacture of Hall China ware begins with flint, feldspar and many different clays, in powder form. These materials are proportioned by weighing. After being weighed, they are fed into a mixing machine containing water.

Figure 1 shows the process flow from raw materials through finished product at the Hall China Company.[1]

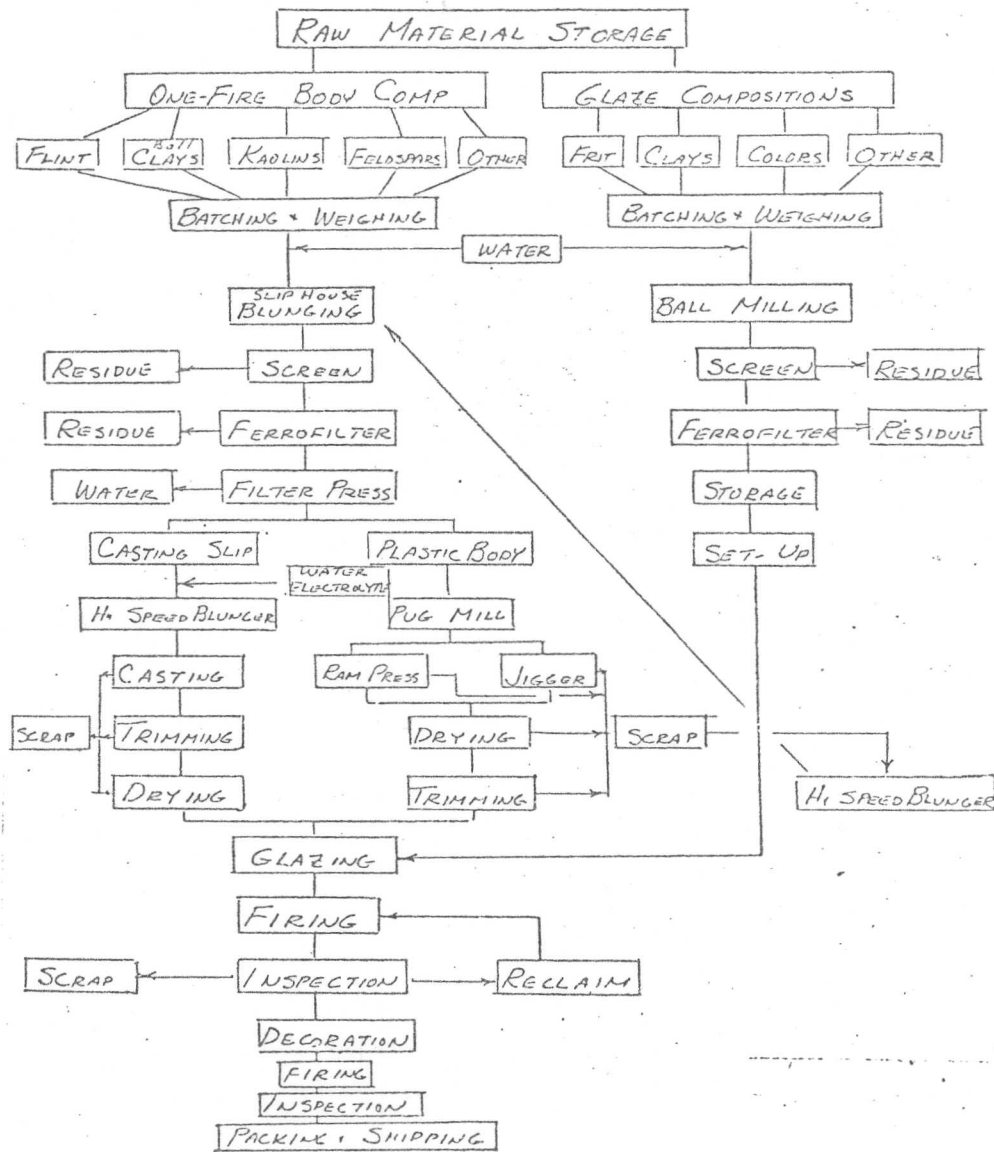

Figure 1. Hall China Company Plant Flow Sheet

(1)(Diagram supplied courtsey of Hall China Co.)

IH AND MEDICAL PROGRAM

In 1975, Jack Rainear, a ceramic engineer at Hall China Company, was trained by the Industrial Health Foundation, Inc. (IHF), how to conduct industrial hygiene surveys of the plants' facilities and operations. He is still conducting these surveys on an "as-needed" basis. IHF analyzes the collected samples. Dr. Daniel C. Brown, M. D., President of IHF, has evaluated the Hall China Company's medical program with Mrs. Anna K. Carnahan, R. N., plant nurse and personnel director. A local physician, Dr. Ross, devotes approximately one hour per week to the medical program at the Hall China Company. He also serves as the "company doctor" for several other ceramic industry manufacturing plants in the East Liverpool area and is quite familiar with the injuries and illnesses common to the overall ceramics industry.

Each employee has a chest x-ray every two years. The x-rays are taken in the plant dispensary and are read by Mrs. Carnahan. There have been no silicoses cases identified with Hall China Company employment in the last 10 years. Mrs. Carnahan also performs pulmonary function tests on all employees.

DESCRIPTION OF CONTROLS

Local exhaust systems, as well as hoods with dedicated exhaust systems, are being used on those operations that generate the most airborne contaminants. Some of the exhaust systems discharge into bag-type collectors and others onto the roof or to other isolated areas. The accumulation of settled dust observed on flat surfaces throughout the plant did not appear to be excessive. The dustiest conditions were noted in the batch plant where bulk and boxcar-type railroad cars are unloaded and the raw materials are moved in and out of storage bins. The employees are provided with 3M disposable dust respirators. There were no operations in process in the batching area at the time we walked through.

The housekeeping in general appeared to be pretty well under control. However, in the areas where the casters pour "slip" in and out of moulds, the floor may become very cluttered and dusty. Dr. Beals said that past noise level surveys have not identified exposures in excess of the 90 dBa TWA.

In the event of a "wreck" inside the tunnel kilns, the essential personal protective equipment (heat resistant coveralls, shoes, and air-supplied respirators) are available. However, Dr. Beals advised that in the 10 years he's been at the Hall China Company no "wreck" necessitating its use have occurred.

CONCLUSIONS AND RECOMMENDATIONS

Dr. Beals gave the NIOSH visitors (R. Mahon, F. Godbey, W. Jones, and J. Gamble) an excellent tour of the Hall China Company's East Liverpool, Ohio facilities and operations. As a result, we all gained a good understanding of the equipment, processes, and skills inherent to a labor intensive manufacturer of chinaware. If it is decided, after we have looked at other facilities and operations, that our control technology assessment of the ceramics (clay) industry should include this type of operation, this plant

should be a strong candidate for an in-depth study. The medical records the plant develops, evaluates, and files should also make it worthy of serious consideration by the Division of Respiratory Disease Studies (DRDS) for inclusion in their study. The union was most cooperative and they have records and some ongoing research with NCI and the American Standard Corporation that should also be most helpful to DRDS in their study.

Origin and Composition[1]

Most of the earth's crust is composed of a relatively small number of elements. Oxygen, silicon, and aluminum represent 82.7% by weight of the earth's crust. The ten most abundant elements, which comprise 99.2%, are listed in Table 1.

Table 1. Elements in the earth's crust: the top ten.

Element	Weight %	Element	Weight %
Oxygen	49.5	Sodium	2.6
Silicon	25.7	Potassium	2.4
Aluminum	7.5	Mangnesium	1.9
Iron	4.7	Hydrogen	0.9
Calcium	3.4	Titanium	0.6

Silicate minerals contain a basic unit in which each silicon atom is bonded to four oxygen atoms in a tetrahedral arrangement.

More complex silicate structures generally are found in which the tetrahedral silicate units share oxygen atoms. Thus, two tetrahedral units with a shared oxygen would have the formula $Si_2O_7^{6-}$ (Figure 2). It is possible to have a single strand silicate in which the neighboring tetrahedra each share two oxygen atoms to form a long chain. In a similar manner it is possible for each tetrahedral unit to share three or even all four oxygen atoms and form two dimensional sheet type structures or three dimensional arrays.

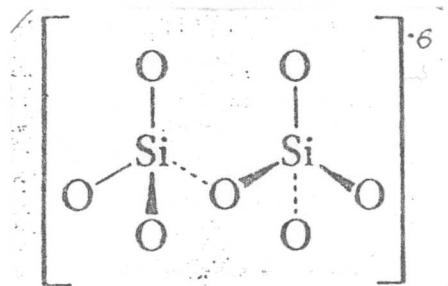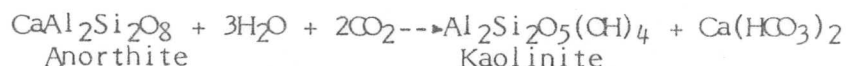[1]Denio, A.A. "Chemistry for Potters," Journal of Chemistry Education, 57:4, April 1980.
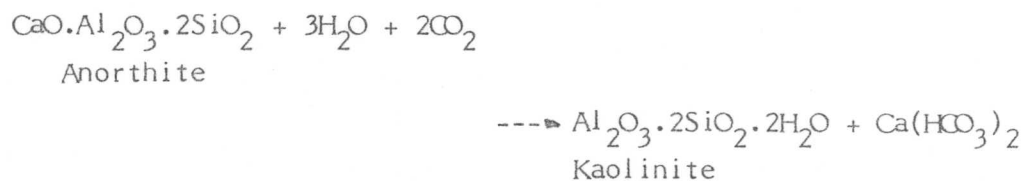
Figure 2. The $Si_2O_7^{6-}$ ion.

Fortunately for potters, some silicate minerals contain Al^{3+} ions in place of the more hazardous Si^{4+} ions in the silicate tetrahedra. The difference in charges is compensated for by the inclusion of other cations such as Na^+, K^+, Ca^{2+}, Mg^{2+}, and Fe^{3+} in the structure. These minerals are called aluminosilicates, a common example being a type of mica with the name muscovite, $KAl_2(AlSi_3O_{10})(OH)_2$. The feldspar minerals are also aluminosilicates and make up about 54% of the earth's crust. One common type of feldspar is anorthite, which has the formula $CaAl_2Si_2O_8$. The basic repeat unit in this mineral is $Al_2Si_2O_8^{2-}$; the Ca^{2+} ions maintain electrical neutrality.

It is believed that clays are formed by the slow weathering of feldspar minerals. Consider the conversion of anorthite into clay by the very slow reaction with water and carbon dioxide.

$$CaAl_2Si_2O_8 + 3H_2O + 2CO_2 \longrightarrow Al_2Si_2O_5(OH)_4 + Ca(HCO_3)_2$$
$$\text{Anorthite} \qquad\qquad\qquad \text{Kaolinite}$$

The first product is the clay mineral kaolinite. Thus, the feldspar mineral anorthite is slowly converted into this clay mineral and calcium bicarbonate; as the latter product is washed away small, hexagonal shaped plate-like crystals of the kaolinite remain. The ratio of the length to thickness of these plates is about 10:1, and the average particle diameter is in the 0.1-100 um range.

The previous paragraph gives the chemical formulas of anorthite and kaolinite as written by chemists. However, potters have traditionally used a different approach in which the minerals are considered to be composed of oxides. The previous chemical equation is preferentially written by potters as:

$$CaO.Al_2O_3.2SiO_2 + 3H_2O + 2CO_2$$
$$\text{Anorthite}$$

$$\longrightarrow Al_2O_3.2SiO_2.2H_2O + Ca(HCO_3)_2$$
$$\text{Kaolinite}$$

This "ideal" formula for clay is given the mineral name kaolinite. The clay that is found in deposits in the earth's crust normally contains many impurities which can alter the color and other properties of the material.

In Table 1, the ten most abundant elements in the earth's crust were presented. It is noted that oxygen is by far the predominant element. If the other nine elements are assumed to be present as oxides, a simple calculation leads to the weight percentages of these oxides in the earth's crust. This assumption ignores the presence of $NaCl$ (halite), CaF_2 (fluorite), and FeS_2 (pyrite) deposits. Chlorine accounts for only about 0.2% by weight of the earth's crust, and fluorine and sulfur are even less common.

The nine most abundant oxides are given in Table 2, along with the weight percentages of the oxide in kaolinite and two typical clay samples, North Carolina kaolin and common red clay. It should be noted that the natural kaolin sample has a composition very close to that of the "theoretical" composition of kaolinite, while the red clay sample approximates the earth's crust rather closely.

The term "clay" has many definitions, depending upon the perspective taken. Thus, a potter, a chemist, and a geologist might have trouble in arriving at a common statement. The American Ceramic Society has provided the following:

"Clay is a fine-grained rock which, when suitably crushed and pulverized, becomes plastic when wet, leather-hard when dried and on firing is converted to a permanent rock-like mass."

This "ceramic" clay is composed of clay minerals and impurities. the clay minerals include kaolinite, illite, chlorite, smectite, and several others. The impurities include quartz, a large variety of iron compounds, several alkali and alkaline earth metal oxides, calcium and magnesium carbonates and sulfates, organic materials, and many more. Clay compositions vary widely, even when taken from a single location. It is little wonder then that these incredibly complex mixtures are not easily defined.

Properties

The plasticity of clay, or its ability to be manipulated when wet, is a complex phenomenon. There are several relevant factors such as: the nature of the very small hexagonal plate crystals having a tremendous amount of surface area per gram; the type of cations adsorbed onto the clay surface; the unique high surface tension of water, and the temperature of the system. It is often necessary to combine different types of clays to obtain suitable working properties.

Aging

The aging of clay to improve its plasticity and workability adds to the mystique of the process. Since clay has been formed slowly over countless centuries, it seems strange that it should need an aging period of a couple of weeks. It appears that a bacterial process is responsible for this clay "ripening" stage. This is favored by keeping the wet clay relatively warm and

by adding a small amount of starch to feed the bacteria. When a new batch of clay is mixed, it is common to add a portion of previously aged clay, which in turn promotes the bacterial process in the new material.

Firing

After a clay body has been formed, it is set aside to dry before the firing process, which is used to form a hard and strong mass. Several changes occur during "firing", and the temperatures for different processes depend to some extent upon the origin of the clay sample.

Residual water in the structure is removed in the 100 to 125°C (212-256°F) range. The chemically combined or OH lattice water (14% in kaolinite) is removed from about 350 to 525°C (662 - 977°F).

Quartz is a normal component of clays, and a phase change or quartz inversion occurs at 573°C (1063°F). At this temperature the more random alpha form changes to the more orderly beta-quartz with a slight volume increase. Most clay samples will contain some organic matter which is burned off in the firing cycle, assuming an adequate supply of air is present. This oxidation process proceeds at a variety of temperatures from 200 to 1,000°C, (392 - 1832°F) depending upon the types of organic residues present.

Table 2. Clay compositions: weight percentages.

Oxides	Kaolinite	North Carolina Kaolin	Common red clay	Earth's crust
SiO_2	46.6	46.2	57.0	55.0
Al_2O_3	39.5	38.4	19.2	14.2
H_2O	13.9	13.2	3.5	8.1
Fe_2O_3		0.6	6.7	6.7
MgO		0.4	3.1	3.2
CaO			4.3	4.8
Na_2O		1.2	2.4	3.5
K_2O			2.0	2.9
TiO_2			0.9	1.0
Others			0.9	0.6
	100.0	100.0	100.0	100.0

Magnesium carbonate is decomposed to the magnesium oxide and carbon dioxide at 790°C (1454°F), while calcium carbonate undergoes a similar change at 880°C (1616°F). The calcium and magnesium sulfates dissociate in the 1,100 to 1,300°C (2012 - 2372°F) range.

When a kaolin sample is fired to almost the complete dehydration point, a slight change in the structure results in the new product called metakaolin. Its exact structure is not well understood. Further heating eventually leads to a defect spinel-type structure at about 950°C (1742°F). In the 1,000 to 1,250°C (1832 - 2282°F) range, long needlelike crystals of mullite $(3 Al_2O_3 2SiO_2)$ are formed. These enhance the strength of the structure.

The alpha and beta quartz transition at 573°C (1063°F) is eventually followed by the formation of tridymite at 870°C (1588°F) and finally cristobalite at 1,470°C (2678°F). These solid phase transitions occur slowly, and the quartz usually remains as cristobalite after cooling to room temperature.

The firing process must be done slowly to permit these several changes to occur without damaging the clay body. The initial "green ware," having very little strength, is transformed into a fired piece that is very hard, strong, resistant to abrasion and having good chemical inertness. About 5 to 10% shrinkage occurs during this process.

Kiln temperatures are very important to the potter, but of greater value is the "heat work", a combination of temperatures and time. The kiln is often equipped with a thermocouple, but most potters still resort to using pyrometric cones to estimate the "heat work" quantity. These cones are slender, three-sided pyramids of known refractoriness values. When a cone of a chosen value bends so that its tip reaches the level of its base, a certain combination of temperature and time associated with that cone has been reached, and the firing is completed.

Glazing

A ceramic glaze is a thin glass layer applied to a pottery surface during a firing process in a kiln. The chemistry involved in glaze formation differs only slightly from that used in the manufacture of glass. One important difference is the need to maintain a higher viscosity of the molten glaze to prevent it from flowing off the pottery surface.

Silica, SiO_2, is the basis for glass formation. However, it has a melting temperature of about 1,710°C (2930°F). Normally one or more flux materials are added to significantly lower the melting temperature of silica. Since SiO_2 is a nonmetal oxide and therefore acidic, metal oxides such as those of the Groups IA and IIA are commonly used. For example, silica mixed with Na_2O (25% by weight) melts at 780°C. If silica is heated with K_2O (23% by weight) and Na_2O (8% by weight), melting occurs at 540°C (1004°F).

Lead(II) oxide or litharge (the potter's name) is an excellent fluxing agent, producing a glaze with many superior properties. These lead containing glazes usually are smooth and clear, adhere well to the pottery surface and interact well with oxides used to provide color. Another lead compound often preferred is $2PbCO_3.Pb(OH)_2$ or white lead. However, there are health problems with these glazes which will be covered later.

Boric oxide is also a commonly used flux which helps to reduce the coefficient of expansion of the glaze. Since it is water soluble, it is usually added to a glaze in the form of the mineral colemanite, $2CaO.3B_2O_3.5H_2O$.

Alumina is used in small amounts in glazes as a stiffening agent or viscosity booster. It helps to prevent the glaze from "running" while in the molten state. It also reduces the tendency for glazes to crystallize on cooling. The alumina is added in the form of kaolin which contains fairly pure kaolinite, $Al_2O_3.2SiO_2.2H_2O$.

A glaze serves to improve the utilitarian qualities and the appearance of pottery. A very important glaze quality is color. The potter can produce a complete spectrum of colors by using only eight metals (titanium, vanadium, chromium, manganese, iron, cobalt, nickel, and copper). In a few special cases, gold, cadmium, and uranium are used: the nonmetals antimony and selenium yield a few unique colors. Thus, only 13 elements are used to provide almost an infinite color range.

The metals can be added as the oxides when convenient, but they are frequently present in other forms. For example, cobalt(II) carbonate is used, rather than the oxide, due to its fine particle size. During the firing process, the carbonate decomposes to the metal oxide and carbon dioxide.

A given element can often produce a variety of colors, depending on several factors. The oxidation state of the metal is of major importance. Copper in the +2 (cupric) state produces blue or green shades, but it gives a red color in the cuprous form (+1). The amount of element used, normally in the 0.5-5% by weight range, determines color depth. The metals present from the fluxing agents are capable of influencing the observed color. Lead in the presence of Cu^{2+} produces a green color, while sodium or potassium yield a blue with the same cation. A boron flux with Cu^{2+} gives a greenish turquoise color. Other color related factors include the amount of alumina, firing temperature, and the presence of an opacifer.

The glaze is prepared as an aqueous suspension, so all ingredients must be finely divided and insoluble. This suspension can be sprayed or painted onto the pottery surface, or the piece can be dipped into the suspension. The glaze is then allowed to dry before it is placed into the kiln for firing.

Chemistry

Few potters understand the chemical definitions of oxidation and reduction. They refer to oxidation as a type of firing cycle during which the kiln dampers are open to provide an adequate supply of air. Reduction is then the opposite condition, when the kiln dampers are closed to prevent or limit the air entering.

Copper provides an important example of redox chemistry. When an oxidation firing is used with a copper-containing glaze, a blue to green color is obtained due to the copper(II) state. A reduction firing yields a red glaze, attributed to copper(I).

Clever potters also resort to an internal reducing agent such as silicon carbide. This compound can be included in a copper-containing glaze which is then fired under oxidation conditions. The final glaze is red due to the reduction of Cu^{2+} to cu^{1+} by the silicon carbide.

Luster glazes are very thin films of metals or metallic oxides (often gold or silver) deposited on previously glazed pottery. One technique involves combining the metallic salt with an organic medium and solvent. This mixture is then painted or sprayed onto the surface to be decorated. During the firing process 600-800°C, (1112 - 1472°F). The metallic ions are reduced by the carbon monoxide generated by the organic matrix. A second approach is to fire the overglaze in a reducing atmosphere, rather thn use the organic binder as the reducing agent.

An American version of the classic Japanese Raku technique also involves a reduction process. A specially prepared glazed pot is fired to a deep red color, then carefully and quickly removed and plunged into a covered container filled with organic matter such as straw, sawdust, or oil. The pot will acquire a smoked appearance, and a copper glaze will give either a red color due to $Cu(I)$ or a luster glaze due to metallic copper.