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Spinks, J. L.

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J. L. Spinks, Danielson, J. A. (ed.),

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FRIT MANUFACTURING
AP-42 Section 8.12
Reference Number
2

# AIR POLLUTION ENGINEERING MANUAL

(1967 ed.)

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service

chine. These particles should not be allowed to fall into the mold. Optimum results are obtained by flood lubrication of the delivery system to the maximum amount that can be handled by a runoff wire or blown off by air. Dry lubrication of delivery systems has been tried on an experimental basis by coating the metal contact surfaces with molybdenum disulfide or graphite.

Although future developments in the application of emulsions to molds look promising, present practice still relies upon mixtures of hydrocarbon greases, oils, and graphite. Silicone emulsions and soluble oils eliminate smoke, but several difficulties must be overcome before they can be widely used for mold lubrication. Water emulsions with their high specific heat cause excessive cooling if they are not applied evenly to the mold surfaces by proper atomization. Fine sprays meet with wind resistance, and these sprays cannot be effectively directed to cover the shoulder sections of some molds. Because of the low viscosity of water emulsions, the emulsions are very difficult to meter through existing sight oil feeders. One company has equipped its machine with individual positive-displacement pumps for each nozzle. Invert-post cross-spraying is found to be most effective in giving a uniform coating to the molds of I. S. machines (Bailey, 1957).

Rotating machines are much easier to lubricate than are individual section machines. Emulsion sprays are most effective on rotating machines when mounted at the point of transfer of gobs from the blank mold to the blow mold.

## FRIT SMELTERS

### INTRODUCTION

Ceramic coatings are generally divided into two classes, depending upon whether they are applied to metal or to glass and pottery. In the case of metal, the coating is widely referred to in this country as porcelain enamel. The use of the term vitreous enamel seems to be preferred in Europe. Glass enamel is sometimes used interchangeably with both terms. On the other hand, the coating applied to glass or pottery is known as ceramic glaze.

Ceramic coatings are essentially water suspensions of ground frit and clay. Frit is prepared by fusing various minerals in a smelter. The molten material is then quenched with air or water. This quenching operation causes the melt to solidify rapidly and shatter into numerous small glass particles, called frit. After a drying process, the frit is finely ground in a ball mill, where other materials are added. When suspended in a solution of water and clay, the resulting mixture is known as a ceramic slip. Enamel slip is applied to metals and fired at high temperatures in a furnace. Glaze slip is applied to pottery or glass and fired in a kiln.

#### Raw Materials

The raw materials that go into the manufacture of various frits are similar to each other whether the frit is for enameling on steel or aluminum or for glazing. The basic difference is in the chemical composition.

The raw materials used in enamels and glazes may be divided into the following six groups: Refractories, fluxes, opacifiers, colors, floating agents, and electrolytes (Andrews, 1961). The refractories include materials such as quartz, feldspar, and clay, which contribute to the acidic part of the melt and give body to the glass. The fluxes include minerals such as borax, soda ash, cryolite, fluorspar, and litharge, which are basic in character and react with the acidic refractories to form the glass and, moreover, tend to lower the fusion temperatures of the glasses. These refractory and flux materials chiefly comprise the ingredients that go into the raw batch that is charged to the smelter.

Materials falling into the other four groups are introduced later as mill additions and rarely exceed 15 percent of the total frit composition. They include opacifiers, which are compounds added to the glass to give it an opaque appearance such as the characteristic white of porcelain enamels. Examples are tin oxide, antimony oxide, sodium antimonate, and zirconium oxide. The color materials include compounds such as the oxides of cobalt, copper, iron, and nickel. The floating agents consist of clay and gums and are used to suspend the enamel or glaze in water. Electrolytes such as borax, soda ash, magnesium sulfate, and magnesium carbonate are added to flocculate the clay and further aid the clay in keeping the enamel or glaze in suspension (Parmelee, 1951).

#### Types of Smelters

Smelters used in frit making, whether for enamel or glaze, may be grouped into three classes: Rotary, hearth, and crucible. The rotary smelter is cylindrical and can be rotated in either direction to facilitate fusing, as shown in Figure 537. It can also be tilted vertically for the pouring operation, as demonstrated in Figure 538. The smelter is open at one end for the introduction of fuel and combustion air. It is similarly open at the opposite end for the discharge of flue gases and for charging raw mate-

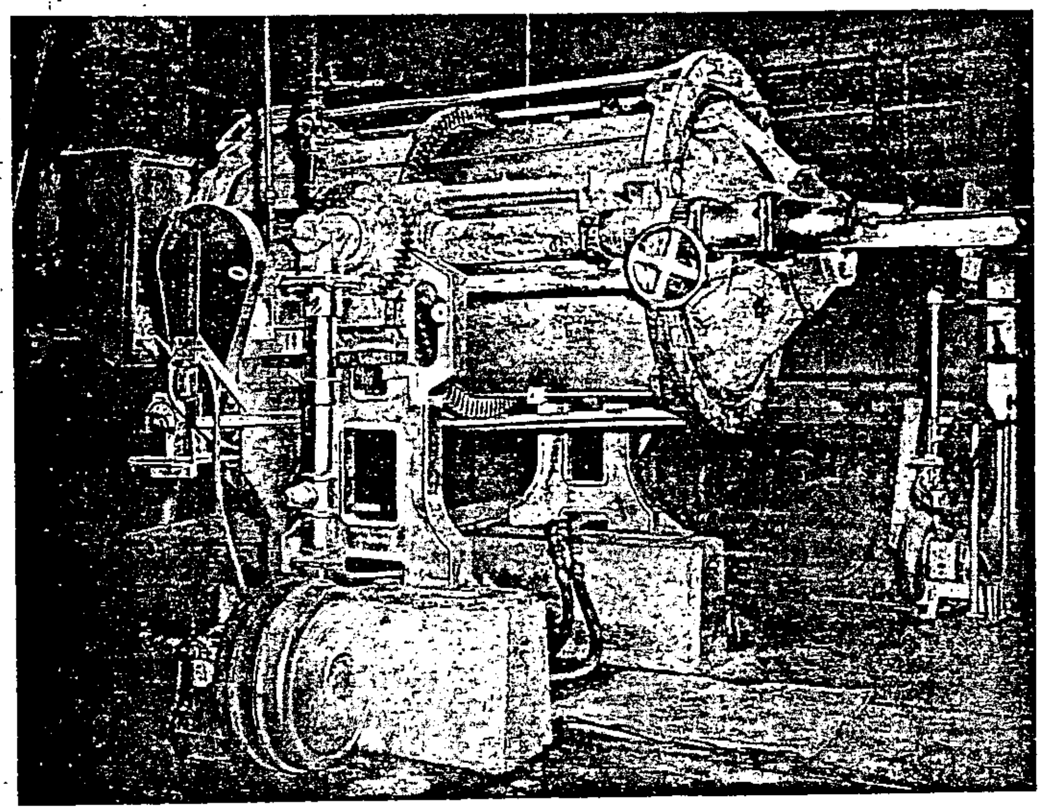

Figure 537. Rotary-type frit smelter (Ferro Corp., Los Angeles, Calif.).

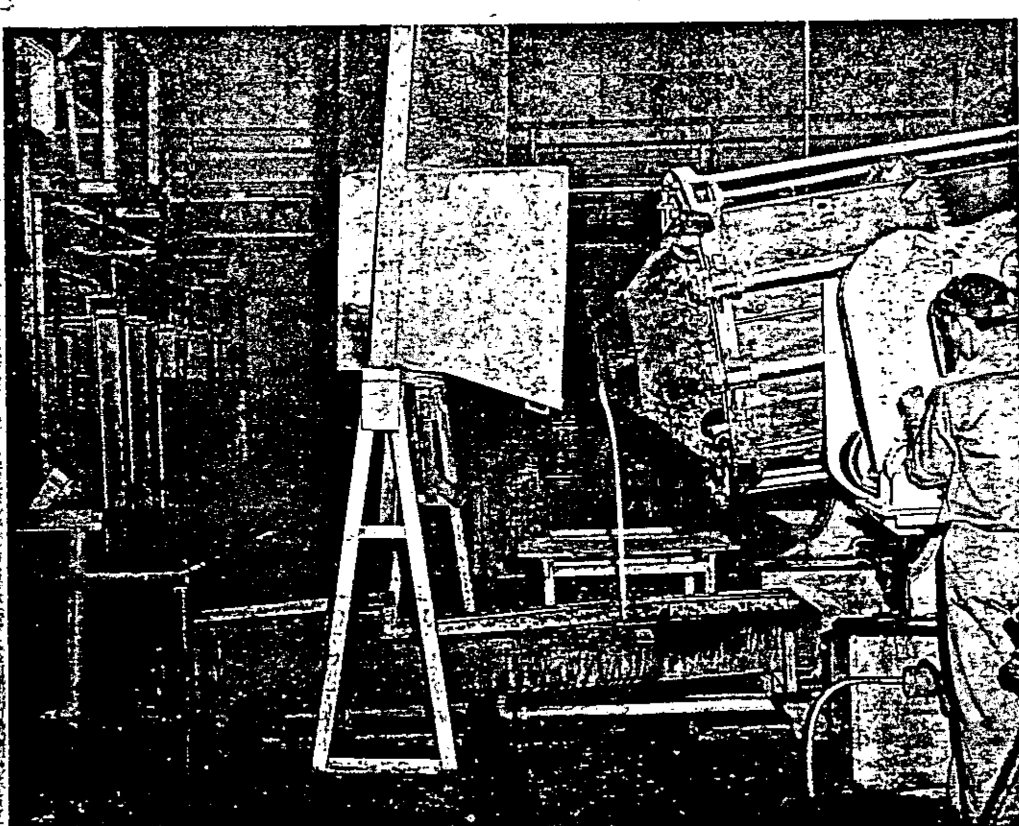

Figure 538. Rotary-type frit smelter in pouring position (Ferro Corp. Los Angeles, Calif.)

rials. Operated solely as a batch-type smelter, it is normally charged by means of a screw conveyor, which is inserted through the opening. Rotary smelters are normally sized to take batches varying from approximately 100 to 3,000 pounds. Fired with either gas or oil, the smelter is lined with high-alumina, refractory firebrick with an average life of from 400 to 600 melts. Firing cycles vary from 1 to 4 hours.

The hearth smelter consists of a brick floor, on which the raw materials are melted, surrounded by a boxlike enclosure. This type of smelter can be either continuous, as illustrated in Figure 539, or batch type, as shown in Figure 540. In either case, the hearth (or bottom) is sloped from one side to a point on the opposite side where the molten material is tapped. The continuous type is usually screw fed. A flue stack is located on the opposite end. Oil or gas is normally used as fuel for the one or more burners. The walls and floor are lined with a first-quality, refractory firebrick. The batch type is sized to take batches ranging from 100 to several thousand pounds. About 30 pounds of batch can be smelted for each square foot of hearth area. The typical continuous-hearth smelter can process 1,000 to 1,500 pounds of raw materials per hour.

The crucible smelter consists of a high-refractory, fireclay, removable crucible mounted within a circular, insulated, steel shell lined with high-grade firebrick, as shown in Figure 541. Heating is usually accomplished with oil or gas burners, though electricity can be used. The combustion chamber surrounds the crucible, occupying the space between the crucible and the shell lining. Because the heat must be transmitted through the crucible to the batch, refractory and fuel costs are high. Crucibles can be sized to smelt a 5-pound batch for laboratory purposes, but the commercial crucibles are sized to take batches from 100 pounds to 3,000 pounds. Smelting cycles vary from 2 to 3 hours at temperatures around 2,200°F, depending upon the size of the batch and its composition. The steel shell is supported by trunnions so that the crucible can be tilted for the pouring operation.

## Frit Manufacturing

Since the raw materials that comprise the smelter batch consist of refractories and fluxes, thorough and uniform mixing of these ingredients before the charging operation is essential for efficient smelting. Smelting involves the heating of raw materials until a fairly homogeneous glass is formed. The fundamental changes that occur are interaction of acids and bases, decomposition, fusion, and solution. A considerable quantity of steam is evolved as the borax begins to melt. The order of melting for some of the materials is: Sodium nitrate at 586°F, borax at 1,366°F, soda ash at 1,564°F, litharge at 1,630°F, feldspar at 2,138°F, and quartz at 3,110°F.

If white or light-colored frits are being smelted, smelter refractory linings must be high in alumina and low in iron to prevent discoloration and dark specks in the frit. The batch is protected from contact with fuel gases during the early stages of smelting by the evolution of gases within the smelter. To illustrate, a batch containing 35 percent borax and 10 percent soda ash loses about 165 pounds of water and 42 pounds of carbon dioxide for a 1,000-pound batch of frit. This is equivalent to 483 cfm water vapor and 60 cfm $CO_2$ at a smelter temperature of 1,700°F and for a smelting period of 30 minutes.

The rate and period of heat application is critical in smelting enamels and glazes. A temperature too low may be sufficient only to vaporize the more fusible materials instead of volatilizing them, and thereby result in a very slow reaction with the more refractory ingredients. A higher operating temperature eliminates this low production rate. If the batch is heated too rapidly, however, the more fusible elements are melted and volatilized before they have a chance to react with the more refractory materials. Driving off the fluxes in this manner results in a harder (less fusible) final batch. Excessive smelting, after the melt is ready to pour, results in a similar condition and, if permitted to continue, necessitates a further increase in temperature to facilitate pouring. Oversmelting also causes loss of opacity, poor gloss, and discoloration in the frit. Insufficient smelting, on the other hand, causes blistering, loss of acid resistance, and poor texture in the finished coating. Batch composition is the determining factor in selecting optimum smelter temperatures and cycles.

After the smelting operation, the molten material is quenched. Rapid cooling can be accomplished with either air, water, or a combination of the two. Air quenching produces a better product but is not normally practiced, owing to the quenching and storage space required. Water quenching is commonly practiced in the industry by pouring the molten material from the tilted smelter into a large pan of water. Water quenching is also frequently done by pouring molten material into a metal trough in which a continuous stream of water is flowing. The trough empties into a large wire basket suspended in a well, which holds the shattered frit but permits the

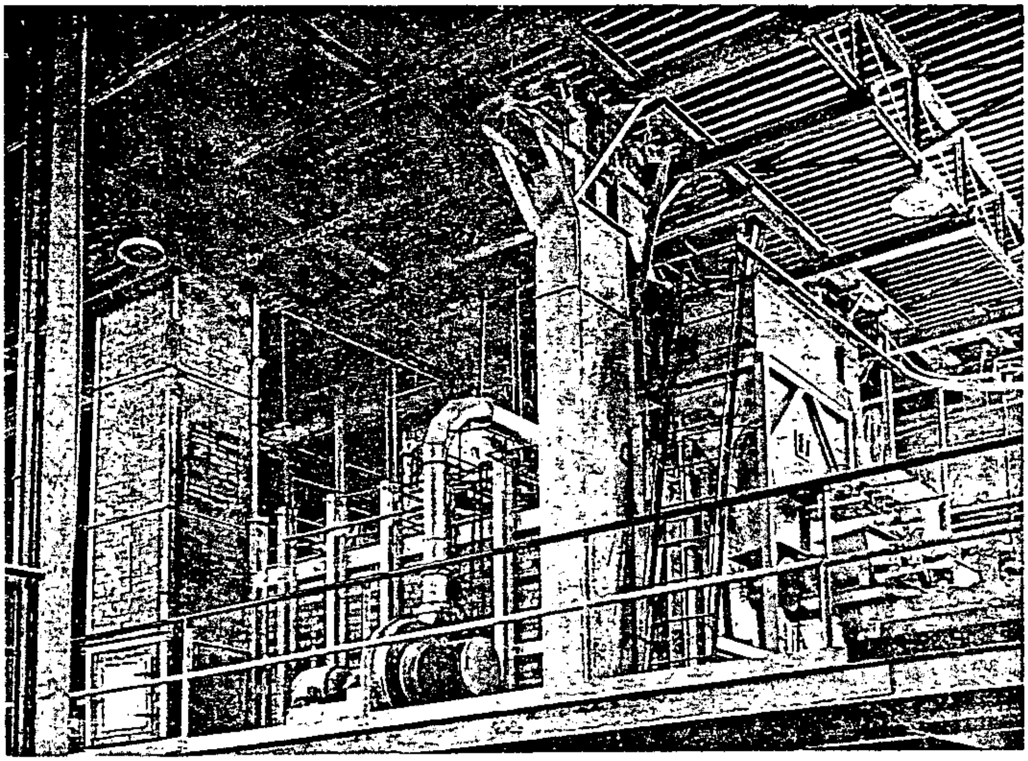

Figure 539. Continuous-hearth-type frit smelter (Ferro Corporation, Los Angeles, Calif.).

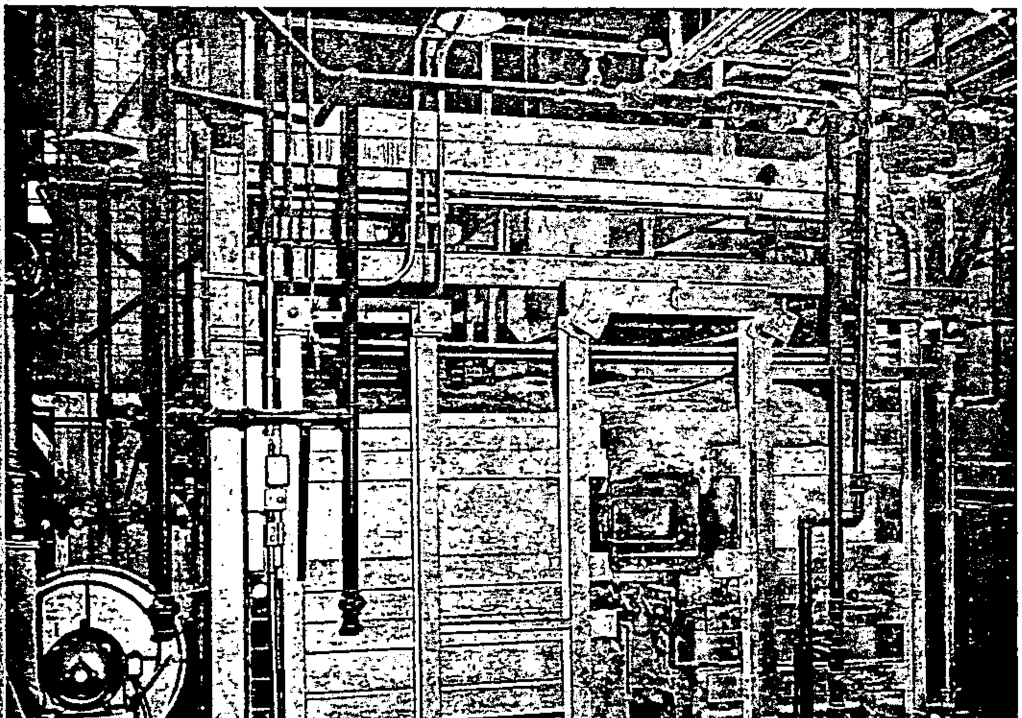

Figure 540. Batch-hearth-type frit smelter (Ferro Corporation, Los Angeles, Calif.).

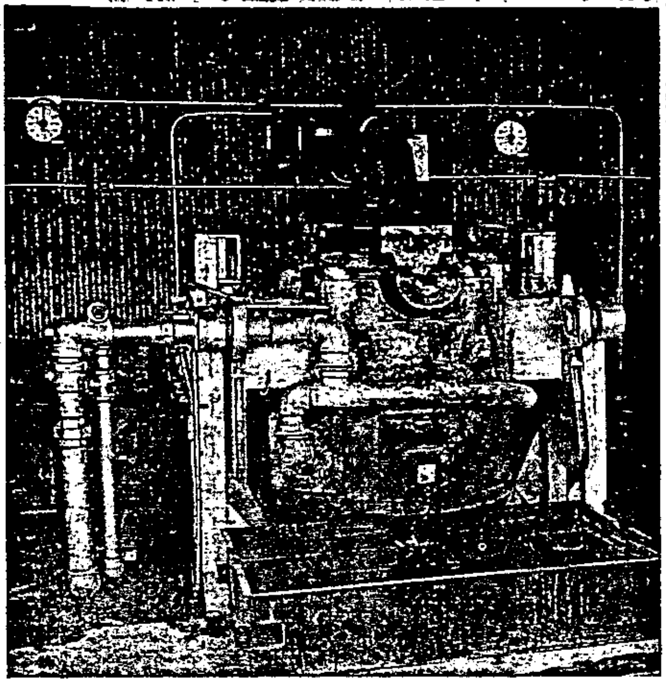

Figure 541. Crucible-type frit smelter (California Metal Enameling Company, Los Angeles, Calif.).

water to flow out through an overflow. Rapid cooling is somewhat impeded by this method owing to a layer of steam that forms over the glass. Air-water quenching appears to be the most economical and effective method since a more thorough shattering of the glass results. In this method the molten material is poured from the smelter and passed through a blast of air and water. Quenching causes the molten material to solidify and shatter into numerous small glass particles (called frit) ranging from 1/4 inch in diameter down to submicron sizes. Its main purpose is to facilitate grinding.

After draining, the frit contains 5 to 15 percent water and may be milled in this condition or may first be dried. Three types of dryers are employed: The drying table, the stationary dryer, and the rotary dryer. The drying table is a flat hearth on which the frit is placed. Heat is applied beneath the hearth, and the frit is raked manually. The stationary dryer consists of a sheet iron chamber in which a basket of frit is placed. Heated air from an exchanger on the smelter flue is passed through the basket of frit. The rotary dryer consists of a porcelain-lined rotating cylinder that is inclined slightly, causing the frit to move through continuously. The typical size is approximately 2 feet in diameter and 20 feet long, though larger cylinders are used. The rotary dryer, which is economical and efficient, can be heated by waste heat or by oil or gas. The frit can be further refined by using magnetic separation to remove small iron particles, which would otherwise cause black specks in the enamel.

The final step in frit making is size reduction, which is normally done with a ball mill. Frits used in porcelain enamel are required to pass a No. 100 sieve (150 μ), though a certain percent of fines must remain as residue on a finer sieve. In the case of ceramic glaze frits, a finer grind is necessary. About one-half of a batch must be less than 2.5 microns with the remainder no greater than 10 microns. Efficient milling is best obtained when the speed of rotation is such that the balls ride three-fourths of the way up one side of the cylinder, and the innermost balls slide back down over the outermost balls. This is achieved, for example, at a speed of 25 rpm for a 4-foot-diameter cylinder. Porcelain balls or flint pebbles are used in the mill. The diameter of the balls ranges from 1 to 3 inches, and the charge should be maintained at about 55 percent of the mill volume. Ball wear amounts to 5 to 10 pounds in milling 1,000 pounds of frit.

Colors, opacifiers, floating agents, and electrolytes are mixed with the frit before it is charged to the ball mill. After the milling operation begins, water is added at a constant rate to keep the specific gravity of the slurry (referred to as slip) at the correct value at all times. After the milling operation, the ceramic slip is screened to remove large particles. A 1- to 2-day aging process then takes place at a temperature close to that at which the enamel or glaze is to be applied. Aging is necessary to set up an equilibrium among the clay, frit, and solution. The enamel or glaze slip is now ready for application.

## Application, Firing, and Uses of Enamels

Enamels and glazes may be applied to ware blanks by immersion or spraying (Hansen, 1932). The pouring and brushing methods are seldom employed today. In the dipping operation, the blank is immersed in the slip and then withdrawn and allowed to drain. If the slip is thick, the excess enamel must be shaken from the ware, a process called slushing. Spraying is the application of enamel or glaze slip to ware by atomizing it through an air gun.

After the enamel or glaze has been applied, it must then be burned or fired on the ware to fuse the coating to a smooth, continuous, glassy layer. The firing temperatures and cycles for porcelain enamel on steel and aluminum are approximately 1,500°F (Shreve, 1945) for 5 minutes and 1,000°F for 5 minutes, respectively. Ceramic glaze, however, is fired on pottery at about 2,300°F for several hours or even days.

The firing is accomplished in what is called a furnace in the porcelain enamel industry, and a kiln in the ceramic glaze industry.

Porcelain enamel is used as a protective coating for metals--primarily steel, cast iron, and aluminum. Familiar items are bathtubs, water heater tanks, refrigerators, washing machines, and cooking ranges. Coated aluminum is being used more and more in recent times for signs such as those installed on highways. Ceramic glazes are used as a decorative or protective coating on a wide variety of pottery and glass articles. Examples are lavatory basins, water closets, closet bowls, chinaware, and figurines.

## THE AIR POLLUTION PROBLEM

Significant dust and fume emissions are created by the frit-smelting operation. These emissions consist primarily of condensed metallic oxide fumes that have volatilized from the molten charge. They also contain mineral dust carryover and sometimes contain noxious gases such as hydrogen fluoride. In addition, products of combustion, and glass fibers are released. The quantity of these air contaminants can be reduced by following good smelter-operating procedures. This can be accomplished by not rotating the smelter too rapidly, to prevent excessive dust carryover, and by not heating the batch too rapidly or too long, to prevent volatilizing the more fusible elements before they react with the more refractory materials. A typical rotary smelter, for example, discharges to the atmosphere, 10 to 15 pounds of dust and fumes per hour per ton of material charged. In some cases, where ingredients require high melting temperatures (1,500°F or higher), emissions as great as 50 pounds per hour per ton of material have been observed. Depending upon the composition of the batch, a significant visible plume may or may not be present. Tables 214 through 217 indicate the extent of emissions from uncontrolled, rotary frit smelters for various-sized batches and compositions.

## HOODING AND VENTILATION REQUIREMENTS

Rotary smelters require a detached canopy-type hood suspended from the lower end of a vertical stack as shown in Figures 537 and 538. It is suspended far enough above the floor to trap the discharge gases from the smelter when in the horizontal position. Refractory-lined, it is of sufficient size to prevent gases from escaping into the room, its size varying with the size of the smelter. The typical hood opening area ranges from 3 to 5 square feet. The stack should be of sufficient height to obtain good draft--about 20 feet--if it is not vented to air pollution control

Table 214. DUST AND FUME DISCHARGE FROM A 1,000-POUND, ROTARY FRIT SMELTER

| Test data | Test No. | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| Process wt, lb/hr | 174[a] | 174[a] | 174[a] |
| Stack vol, scfm | 1,390 | 1,540 | 1,630 |
| Stack gas temp, °F | 450 | 750 | 900 |
| Concentration, gr/scf | 0.118 | 0.387 | 0.381 |
| Stack emissions, lb/hr | 1.41 | 5.11 | 5.32 |
| CO, vol % (stack condition) | 0.002 | 0.001 | 0.002 |
| $N_2$, vol % (stack condition) | 76.9 | 75.10 | 73.50 |
| | 4 | 5 | 6 |
| Process wt, lb/hr | 292[b] | 292[b] | 292[b] |
| Stack vol, scfm | 1,310 | 1,400 | 1,480 |
| Stack gas temp, °F | 960 | 950 | 930 |
| Concentration, gr/scf | 0.111 | 0.141 | 0.124 |
| Stack emissions, lb/hr | 1.25 | 1.79 | 1.57 |
| CO, vol % (stack condition) | 0 | 0 | 0 |
| $N_2$, vol % (stack condition) | 73 | 72.60 | 73.30 |

[a]These three tests represent approximately the 1st, 2d, and 3d hours of a 248-minute smelting cycle. The total charge amounted to 717 pounds of material consisting of borax, feldspar, sodium fluoride, soda ash, and zinc oxide.

[b]These three tests represent approximately the 1st, 2d, and 3d hours of a 195-minute smelting cycle. The total charge amounted to 949 pounds of material consisting of litharge, silica, boric acid, feldspar, fluorspar, borax, and zircon.

Table 215. DUST AND FUME DISCHARGE FROM A 3,000-POUND, ROTARY FRIT SMELTER

| Test data | Test No. | | |
|---|---|---|---|
| | 7 | 8 | 9 |
| Process wt, lb/hr | 472[a] | 472[a] | 472[a] |
| Stack vol, scfm | 2,240 | 2,270 | 2,260 |
| Stack gas temp, °F | 630 | 800 | 840 |
| Concentration, gr/scf | 0.143 | 0.114 | 0.172 |
| Stack emissions, lb/hr | 2.70 | 2.20 | 3.30 |
| CO, vol % (stack condition) | 0.02 | 0.02 | 0.02 |
| $N_2$, vol % (stack condition) | 75.30 | 75.60 | 76.30 |

[a]These three tests represent approximately the 1st, 2d, and 3d hours of a 248-minute smelting cycle. The total charge amounted to 1,951 pounds of material consisting of litharge, silica, boric acid, feldspar, whiting, borax, and zircon.

Table 216. FLUORIDE DISCHARGE FROM A ROTARY FRIT SMELTER

| Test data | Test No. | | | |
|---|---|---|---|---|
| | 10 | 11 | 12 | 13 |
| Process wt, lb/hr | 174[a] | 174[a] | 162[b] | 162[b] |
| Stack vol, scfm | 1,400 | 1,600 | 1,000 | 1,000 |
| Stack gas temp, °F | 530 | 840 | 480 | 480 |
| Concentration, gr/scf | 0.061 | 0.035 | 0.196 | 0.058 |
| Stack emissions, lb/hr | 0.73 | 0.48 | 1.68 | 0.50 |

[a]These two tests were of 90 minutes' duration each and represented approximately the first half and the second half of a 248-minute smelting cycle. The total charge amounted to 717 pounds of material consisting of borax, feldspar, sodium fluoride, soda ash, and zinc oxide.

[b]These two 60-minute tests represented approximately the 1st and the 4th hours of a 450-minute smelting cycle. The total charge amounted to 1,213 pounds of material consisting of sodium carbonate, calcium carbonate, pyrobar, and silica. The test was specifically conducted for a batch containing maximum carbonates (19%) and no litharge.

Table 217. DUST AND FUME DISCHARGE FROM A 2,000-POUND ROTARY FRIT SMELTER

| Test data | Test No. 14 | 15 | 16 | 17 |
|---|---|---|---|---|
| Process wt, lb/hr | 857[a] | 857[a] | 890[b] | 890[b] |
| Stack vol, scfm | 2,430 | 2,430 | 4,347 | 4,347 |
| Stack gas temp, °F | 600 | 600 | 340 | 340 |
| Concentration, gr/scf | 0.130 | 0.112 | 0.111 | 0.103 |
| Stack emissions, lb/hr | 2.710 | 2.340 | 4.150 | 3.820 |

[a] These two 60-minute tests represent the 1st and 2d hours of a 140-minute smelting cycle. The total charge amounted to 2,000 pounds of material containing silica, litharge, and whiting.

[b] These two 60-minute tests represent the 1st hour and 37 minutes of a 135-minute smelting cycle. The total charge amounted to 2,000 pounds of material containing silica, litharge, and whiting.

equipment. If it is vented to control equipment, ventilation requirements are approximately 3,000 scfm for a 2,000-pound batch smelter as an example. Hood indraft velocity should be about 500 fpm.

Crucible and hearth smelters do not require hoods but do require a 20- or 25-foot stack to conform with good chimney design practice if not vented to air pollution control equipment. Some crucible smelters are vented directly into the room. If vented to air pollution control equipment, a canopy hood must be used on the crucible smelter. Hood indraft velocities should be approximately 200 fpm. The requirement for a hearth- (box-) type smelter is approximately 4,000 scfm for a 3,000-pound batch smelter. As a general rule, about 70 scfm is required for each square foot of hearth area.

## AIR POLLUTION CONTROL EQUIPMENT

The two most feasible control devices for frit smelters are baghouses and venturi water scrubbers. Of these devices, baghouses are more effective. Glass bags cannot be used, however, owing to the occasional presence of fluorides in the effluent. The discharge gases must be cooled by heat exchangers, quench chambers, cooling columns, or by some other device to a temperature compatible with the fabric material selected. Filtering velocities should not exceed 2.5 fpm.

A venturi-type water scrubber is satisfactory if at least 20 to 25 inches of pressure drop is maintained across the venturi throat. The throat velocity should be between 15,000 and 20,000 fpm. The water requirement at the throat is about 6 gpm for each 1,000 cubic feet of gas treated. Power consumption is high owing to the high pressure drop. The venturi scrubber shown in Figure 542 was installed to serve one rotary and two hearth smelters simultaneously. Table 218 includes data indicating the collection efficiency of this scrubber when venting a frit smelter.

A baghouse installation venting four rotary, gas-fired frit smelters is shown in Figure 543. The production capacity of one of the smelters is 3,000 pounds while that of the other three is 1,000 pounds each. Maximum gas temperatures encountered in the discharge stack at a point 20 feet downstream of the smelters are approximately 950°F, while the average temperature is 780°F.

Table 218. EFFICIENCY OF VENTURI WATER SCRUBBER ON PARTICULATE MATTER AND FLUORIDES WHEN VENTING THREE FRIT SMELTERS

| Test data | Test No.[a] 18 | 19 | 20 | 21 | 22 | 23 |
|---|---|---|---|---|---|---|
| | Dust and fumes | | | Fluorides | | |
| Process wt, lb/hr | 1,360 | 1,360 | 1,360 | 1,360 | 1,360 | 1,360 |
| Stack vol, scfm | 4,280 | 4,280 | 4,280 | 4,280 | 4,280 | 4,280 |
| Stack gas temp, °F | 570 | 552 | 564 | 570 | 552 | 564 |
| Dust concentration, gr/scf | | | | | | |
| Inlet | 0.228 | 0.234 | 0.127 | 0.092 | 0.137 | 0.034 |
| Outlet | 0.074 | 0.077 | 0.088 | 0.006 | 0.008 | 0.017 |
| Dust emissions, lb/hr | | | | | | |
| Inlet | 8.37 | 8.60 | 1.78 | 3.38 | 5.03 | 0.48 |
| Outlet | 2.72 | 2.85 | 1.35 | 0.22 | 0.29 | 0.26 |
| Control efficiency, % | 67.50 | 67.20 | 30.70 | 93.20 | 94 | 50 |

[a] Tests No. 18 and 21 represent the first 54 minutes of the 107-minute smelting cycle, tests No. 19 and 22 represent the last 54 minutes, and tests No. 20 and 23 represent the 23-minute tapping period. Total process weight was 3,000 pounds of material consisting of borax, potassium carbonate, potassium nitrate, zinc oxide, titanium oxide, ammonium phosphate, lithium carbonate, sodium silico-fluoride, fluorspar, silica, and talc. Pressure drop across throat was 21 in. WC. Water flow rate to throat was 50 gpm.