AIR POLLUTION

ENGINEERING MANUAL

SECOND EDITION

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COUNTY OF LOS ANGELES

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SECONDARY ZINC-MELTING PROCESSES

Zinc is melted in crucible, pot, kettle, reverberatory, or electric-induction furnaces for use in alloying, casting, and galvanizing and is reclaimed from higher melting point metals in sweat furnaces. Secondary refining of zinc is conducted in retort furnaces, which can also be used to manufacture zinc oxide by vaporizing and burning zinc in air. All these operations will be discussed in this section except the reclaiming of zinc from other metals by use of a sweat furnace. Information on this subject can be found in a following section entitled, "Metal Separation Processes."

ZINC MELTING

The melting operation is essentially the same in all the different types of furnaces. In all but the low-frequency induction furnace, solid metal can be melted without the use of a molten heel. Once a furnace is started, however, a molten heel is generally retained after each tap for the beginning of the next heat.

Zinc to be melted may be in the form of ingots, reject castings, flashing, or scrap. Ingots, rejects, and heavy scrap are generally melted first to provide a molten bath to which light scrap and flashing are added. After sufficient metal has been melted, it is heated to the desired pouring temperature, which may vary from 800° to 1,100°F. Before the pouring, a flux is added and the batch agitated to separate the dross accumulated during the melting operation. Dross is formed by the impurities charged with the metal and from oxidation during the melting and heating cycles. The flux tends to float any partially submerged dross and conditions it so that it can be skimmed from the surface. When only clean ingot is melted, very little, if any, fluxing is necessary. On the other hand, if dirty scrap is melted, large amounts of fluxes are needed. After the skimming, the melt is ready for pouring into molds or ladles. No fluxing or special procedures are employed while the zinc is being poured.

The Air Pollution Problem

The discharge of air contaminants from melting furnaces is generally caused by excessive temperatures and by the melting of metal contaminated with organic material. Fluxing can also create excessive emissions, but fluxes are available that clean the metal without fuming.

Probably the first visible discharge noted from a furnace is from organic material. Before the melt is hot enough to vaporize any zinc, accompanying organic material is either partially oxidized or vaporized, causing smoke or oily mists to be discharged. This portion of the emissions can be controlled either by removing the organic material before the charging to the furnace or by completely burning the effluent in a suitable incinerator or afterburner.

Normally, zinc is sufficiently fluid for pouring at temperatures below 1,100°F. At that temperature, its vapor pressure is 15.2 millimeters of mercury, low enough that the amount of fumes formed cannot be seen. If the metal is heated above 1,100°F, excessive vaporization can occur and the resulting fumes need to be controlled with an air pollution control device. Zinc can vaporize and condense as metallic zinc if existing temperatures and atmospheric conditions do not promote oxidation. Finely divided zinc so formed is a definite fire hazard, and fires have occurred in baghouses collecting this material.

Many fluxes now in use do not fume, and air contaminants are not discharged. In some cases, however, a specific fuming flux may be needed, in which case a baghouse is required to collect the emissions. An example of a fuming flux is ammonium chloride, which, when heated to the temperature of molten zinc, decomposes into ammonia and hydrogen chloride gases. As the gases rise into the atmosphere above the molten metal, they recombine, forming a fume consisting of very small particles of ammonium chloride.

Provided the temperature of the melt does not exceed 1,100°F, there should be no appreciable amounts of air contaminants discharged when the zinc is poured into molds. Some molds, however, especially in die casting, are coated with mold release compounds containing oils or other volatile material. The heat from the metal vaporizes the oils, creating air contaminants. Recently mold release compounds have been developed that do not contain oils, and this source of air pollution is thereby eliminated.

ZINC VAPORIZATION

Retort furnaces are used for operations involving the vaporization of zinc including (1) reclaiming zinc from alloys, (2) refining by distillation, (3) recovering zinc from its oxide, (4) manufacturing zinc oxide, and (5) manufacturing powdered zinc.

Three basic types of retort furnaces are used in Los Angeles County: (1) Belgian retorts, (2) distillation retorts (sometimes called bottle retorts), and (3) muffle furnaces. Belgian retorts are used to reduce zinc oxide to metallic zinc. Distillation retorts, used for batch distillations, reclaim zinc from alloys, refine zinc, make powdered zinc, and make zinc oxide. Muffle furnaces, used for continuous distillation, reclaim zinc from alloys, refine zinc, and make zinc oxide.

Although zinc boils at 1,665°F, most retort furnaces are operated at temperatures ranging from 1,800° to 2,280°F. Zinc vapor burns spontaneously in air; therefore, air must be excluded from the retort and condenser when metallic zinc is the desired product. Condensers are designed, either for rapid cooling of the zinc vapors to a temperature below the melting point to produce powdered zinc, or for slower cooling to a temperature above the melting point to produce liquid zinc. When the desired product is zinc oxide, the condenser is bypassed and the vapor is discharged into a stream of air where spontaneous combustion converts the zinc to zinc oxide. Excess air is used, not only to ensure sufficient oxygen for the combustion, but also to cool the products of combustion and convey the oxide to a suitable collector.

REDUCTION RETORT FURNACES

Reduction in Belgian Retorts

The Belgian retort furnace is one of several horizontal retort furnaces that have been for many years the most common device for the reduction of zinc. Although the horizontal retort process is now being replaced by other methods capable of handling larger volumes of metal per retort and by the electrolytic process for the reduction of zinc ore, only Belgian retorts are used in the Los Angeles area. In this area, zinc ores are not reduced; the reduction process is used to reclaim zinc from the dross formed in zinc-melting operations, the zinc oxide collected by air pollution control systems serving zinc alloy-melting operations, and the contaminated zinc oxide from zinc oxide plants.

A typical Belgian retort (Figure 202) is about 8 inches in internal diameter and from 48 to 60 inches long. One end is closed and a conical shaped clay condenser from 18 to 24 inches long is attached to the open end. The retorts are arranged in banks with rows four to seven high and as many retorts in a row as are needed to obtain the desired production. The retorts are generally gas fired.

The retorts are charged with a mixture of zinc oxide and powdered coke. Since these materials are powdered, water is added to facilitate charging and allow the mixture to be packed tightly into the retort. From three to four times more carbon is used than is needed for the reduction reaction.

After the charging, the condensers are replaced and their mouths stuffed with a porous material. A small hole is left through the stuffing to allow moisture and unwanted volatile materials to escape. About 3 hours are needed to expel all the undesirable volatile materials from the retort. About 6 hours after charging is completed, zinc vapors appear. The charge in the retort is brought up to 1,832° to 2,012°F for about 8 hours, after which it may rise slowly to a maximum of 2,280°F. The temperature on the outside of the retorts ranges from 2,375° to 2,550°F. The condensers are operated at from 780° to 1,020°F, a temperature range above the melting point of zinc but where the vapor pressure is so low that a minimum of zinc vapor is lost.

The reduction reaction of zinc oxide can be summarized by the reaction:

$$ZnO + C = Zn + CO \qquad (101)$$

Very little, if any, zinc oxide is, however, actually reduced by the solid carbon in the retort. A series of reactions results in an atmosphere rich in carbon monoxide, which does the actual reducing. The reactions are reversible, but by the use of an excess of carbon, they are forced toward the right. The reactions probably get started by the oxidation of a small portion of the coke by the oxygen in the residual air in the retort. The oxygen is quickly used, but the carbon dioxide formed reacts with the carbon to form carbon monoxide according to the equation:

$$CO_2 + C = 2CO \qquad (102)$$

The carbon monoxide in turn reacts with zinc oxide to produce zinc and carbon dioxide:

$$CO + ZnO = Zn + CO_2 \qquad (103)$$

Carbon monoxide is regenerated by use of equation 102, and the reduction of the zinc oxide proceeds.

About 8 hours after the first zinc begins to be discharged, the heat needed to maintain production begins to increase and the amount of zinc produced begins to decrease. Although zinc can still be produced, the amount of heat absorbed by the reduction reaction decreases and the temperature of the retort and its contents increases. Care must be taken not to damage the retort or fuse its charge. As a result, a 24-hour cycle has been found to be an economical operation. The zinc values still in the spent charge are recovered by recycling with the fresh charges. A single-pass recovery yields 65 to 70 percent of the zinc charged, but, by recycling, an overall recovery of 95 percent may be obtained.

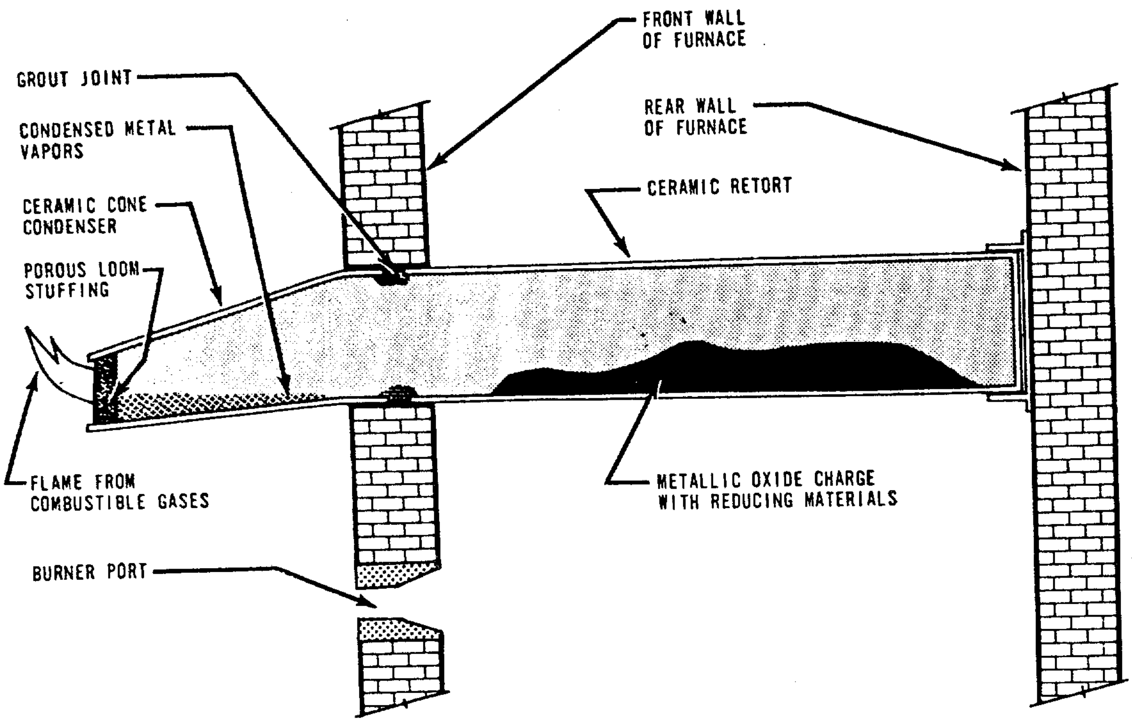

Figure 202. Diagram showing one bank of a Belgian retort furnace.

The Air Pollution Problem

The air contaminants emitted vary in composition and concentration during the operating cycle of Belgian retorts. During charging operation very low concentrations are emitted. The feed is moist and, therefore, not dusty. As the retorts are heated, steam is emitted. After zinc begins to form, both carbon monoxide and zinc vapors are discharged. These emissions burn to form gaseous carbon dioxide and solid zinc oxide. During the heating cycle, zinc is poured from the condensers about three times at 6- to 7-hour intervals. The amount of zinc vapors discharged increases during the tapping operation. Before the spent charge is removed from the retorts, the temperature of the retorts is lowered, but zinc fumes and dust from the spent charge are discharged to the atmosphere.

Hooding and Ventilation Requirements

Air contaminants are discharged from each retort. In one installation, a furnace has 240 retorts arranged in five horizontal rows with 48 retorts per row. The face of the furnace measures 70 feet long by 8 feet high; therefore, the air contaminants are discharged from 240 separate openings and over an area of 560 square feet. A hood 2 feet wide by 70 feet long positioned immediately above the front of the furnace is used to collect the air contaminants. The hood indraft is 175 fpm.

DISTILLATION RETORT FURNACES

The distillation retort furnace (Figure 203) consists of a pear-shaped, graphite retort, which may be 5 feet long by 2 feet in diameter at the closed end by 1-1/2 feet in diameter at the open end and 3 feet in diameter at its widest cross-section. Normally, the retort is encased in a brick furnace with only the open end protruding and it is heated externally with gas- or oil-fired burners. The retorts are charged with molten, impure zinc through the open end, and a condenser is attached to the opening to receive and condense the zinc vapors. After the distillation is completed, the condenser is moved away, the residue is removed from the retort, and a new batch is started.

The vaporized zinc is conducted either to a condenser or discharged through an orifice into a stream of air. Two types of condensers are used — a brick-lined steel condenser operated at from 780° to 1,012° F to condense the vapor to liquid zinc, or a larger, unlined steel condenser that cools the vapor to solid zinc. The latter condenser is used to manufacture powered zinc. The condensers must be operated at a slight positive pressure to keep air from entering them and

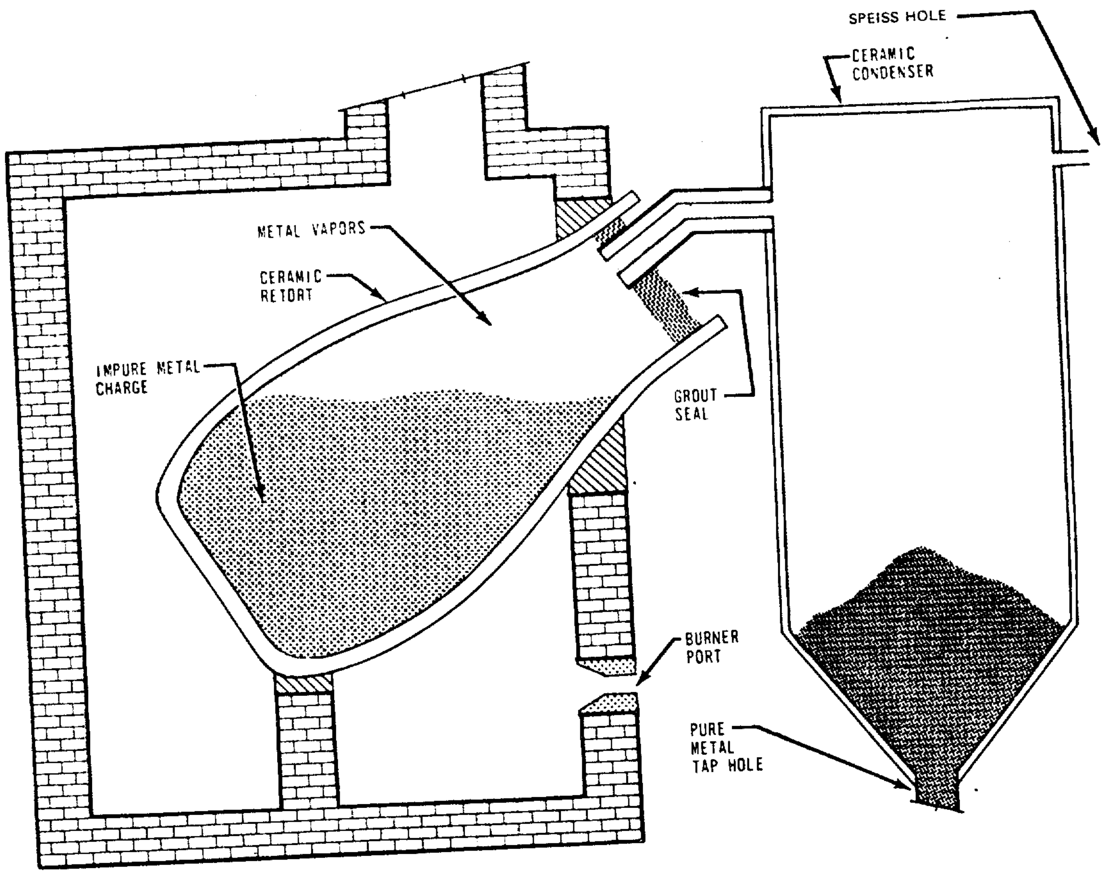

Figure 203. Diagram of a distillation-type retort furnace.

oxidizing the zinc. To ensure that there is a positive pressure, a small hole, called a "speiss" hole, is provided through which a small amount of zinc vapor is allowed to escape continuously into the atmosphere. The vapor burns with a bright flame, indicating that there is a pressure in the condenser. If the flame gets too large, the pressure is too high. If it goes out, the pressure is too low. In either case, the proper adjustments are made to obtain the desired condenser pressure.

When it is desired to make zinc oxide, the vapor from a retort is discharged through an orifice into a stream of air where zinc oxide is formed inside a refractory-lined chamber. The combustion gases and air, which bear the oxide particles, are then carried to a baghouse collector where the powdered oxide is collected.

The Air Pollution Problem

During the 24-hour cycle of the distillation retorts, zinc vapors escape from the retort (1) when the residue from the preceding batch is removed from the retort and a new batch is charged, and (2) when the second charge is added to the retort. As the zinc vapors mix with air, they oxidize and form a dense cloud of zinc oxide fumes. Air contaminants are discharged for about 1 hour each time the charging hole is open. When the zinc is actually being distilled, no fumes escape from the retort; however, a small amount of zinc oxide escapes from the speiss hole in the condenser. Although the emission rate is low, air contaminants are discharged for about 20 hours per day.

Hooding and Ventilation Requirements

To capture the emissions from a distillation retort furnace, simple canopy hoods placed close to and directly over the sources of emissions are sufficient. In the only installation in Los Angeles County, the charging end of the retort protrudes a few inches through a 4-foot-wide, flat wall of the furnace. The hood is 1 foot above the retort, extends 1-1/4 feet out from the furnace wall, and is 4 feet wide. The ventilation provided is 2,000 cfm, giving a hood indraft of 400 fpm. Fume pickup is excellent. The speiss hole is small and all the fumes discharged are captured by a 1-foot-diameter hood provided with 200 cfm ventilation. The hood indraft is 250 fpm.

The retorts are gas fired and the products of combustion do not mix with the emissions from the retort or the condenser. The exhausted gases are heated slightly by the combustion of zinc and from radiation and convection losses from the retort, but the amount of heating is so low that no cooling is necessary.

MUFFLE FURNACES

Muffle furnaces (Figure 204) are continuously fed retort furnaces. They generally have a much greater vaporizing capacity than either Belgian retorts or bottle retorts do,and they are operated continuously for several days at a time. Heat for vaporization is supplied by gas- or oil-fired burners by conduction and radiation through a silicon carbide arch that separates the zinc vapors and the products of combustion. Molten zinc from either a melting pot or sweat furnace is charged through a feed well that also acts as an air lock. The zinc vapors are conducted to a condenser where purified liquid zinc is collected, or the condenser is bypassed and the vapors are discharged through an orifice into a stream of air where zinc oxide is formed.

A muffle furnace installation in Los Angeles County consists of three identical furnaces, each capable of vaporizing several tons of zinc per day. These furnaces can produce zinc of 99.99 percent purity and zinc oxide of 99.95 percent purity from zinc alloys. Each furnace has three sections: (1) A vaporizing chamber, (2) a condenser, and (3) a sweating chamber. Figure 205 shows the feed ends of the furnaces, including the sweating chambers, and some of the ductwork and hoods serving the furnaces.

Each furnace, including the feed well and sweating chamber, is heated indirectly with a combination gas- or oil-fired burner. The combustion chamber, located directly over the vaporizing chamber, is heated to about 2,500°F. On leaving the combustion chamber, the products of combustion are conducted over the zinc feed well and through the sweating chamber to supply the heat needed for melting the zinc alloys from the scrap charged and for heating the zinc in the feed well to about 900°F.

Zinc vapors are conducted from the vaporizing section into a multiple-chamber condenser. When zinc oxide is the desired product, the vapors are allowed to escape through an orifice at the top of the first chamber of the condenser. Even when maximum zinc oxide production is desired, some molten zinc is nevertheless formed and collects in the condenser.

When metallic zinc is the desired product, the size of the orifice is greatly reduced, but not entirely closed, so that most of the vapors enter the second section of the condenser where they condense to molten zinc. The molten zinc collected in the condenser is held at about 900°F in a well, from which it is periodically tapped. The well and the tap hole are so arranged that sufficient molten zinc always remains in the well to maintain an air lock.

The zinc that escapes from the orifice while molten zinc is being made burns to zinc oxide, which is conducted to the product baghouse.

The Air Pollution Problem

Dust and fumes are created by the sweating operation. Scrap is charged into the sweating chamber through the door shown in Figure 205. After the

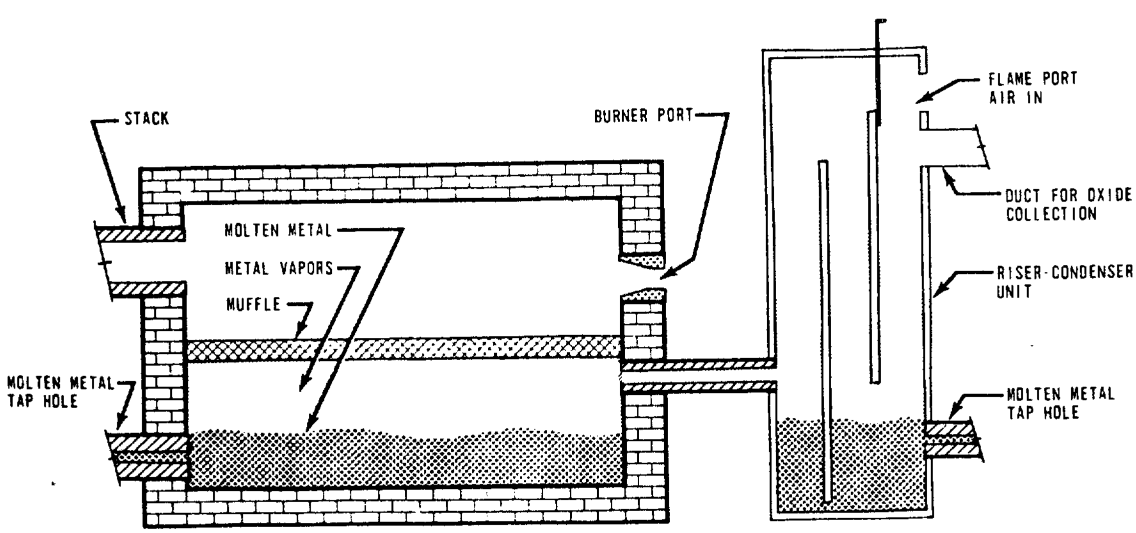

Figure 204. Diagram of a muffle furnace and condenser.

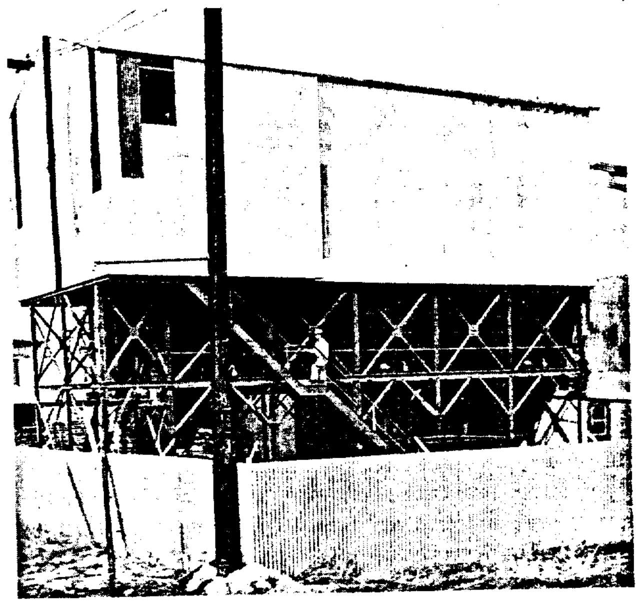

Figure 205. (Left) Zinc-vaporizing muffle furnaces, (right) baghouse for collecting the zinc oxide manufactured (Pacific Smelting Co., Torrance, Calif.).

zinc alloys have been melted, the residue is pushed out of the chamber through a second door and onto a shaker screen where dross is separated from solid metal. Excessive dust and fumes are thereby created.

The zinc alloys charged into the vaporizing section contain copper, aluminum, iron, lead, and other impurities. As zinc is distilled from the metals, the concentration of the impurities increases until continued distillation becomes impractical. After 10 to 14 days of operation, the residue, containing 10 to 50 percent zinc must be removed. When tapped, the temperature of the residue is about 1,900°F, hot enough to release zinc oxide fumes. The molds collecting the residue metal are so arranged that the metal overflows from one mold to another; however, the metal cools so rapidly that fumes are released only from the pouring spout and the first two or three molds. The fumes, almost entirely zinc oxide, are 100 percent opaque from the pouring spout and the first mold. At the third mold, the opacity decreases to 10 percent.

Any discharge of zinc vapor from the condenser forms zinc oxide of product purity; therefore, the condenser vents into the intake hood of a product-collecting exhaust system. Since some zinc oxide is always produced, even when the condenser is set to produce a maximum of liquid zinc, the product-collecting exhaust system is always in operation to prevent air contaminants from escaping from the condenser to the atmosphere.

Hooding and Ventilation Requirements

The dust and fumes created by the charging of scrap and the sweating of zinc alloys from the scrap originate inside the sweat chamber. The thermal drafts cause the emissions to escape from the upper portion of the sweat chamber doors. Hoods are placed over the doors to collect the emissions. The charging door hood extends 10 inches from the furnace wall and covers a little more than the width of the door (see Figure 205). With two furnaces in operation at the same time, each of the charging door hoods is supplied with 3,200 cfm ventilation, which provides an indraft velocity of 700 fpm. All fumes escaping from the charging doors are collected by these hoods.

The unmelted scrap and dross are raked from a sweating chamber onto a shaker screen. A hood enclosing the discharge lip and the screen is provided with 5,500 cfm ventilation. The inlet velocity is 250 fpm, sufficient to capture all of the emissions escaping from both the furnace and the screen.

A hood 3 feet square positioned over the residue metal-tapping spout and the first mold is provided with 8,700 cfm ventilation. During the tapping, no metal is charged to either sweating chamber, and the exhaust system dampers are arranged so that approximately one-half of the available volume is used at the tapping spout. The indraft velocity is in excess of 900 fpm, and all fumes released from the metal are collected, even from the second and third molds up to 6 feet away from the hood.

The ductwork joining the hoods to the control devices is manifolded and dampered so that any or all hoods can be opened or closed. The exhaust system provides sufficient ventilation to control the fumes created by two furnaces in operation at the same time. When residue metal is being tapped from a furnace, no metal is being charged to the other furnaces; therefore, all the ventilation, or as much as is needed, can be used at the tapping hood.

AIR POLLUTION CONTROL EQUIPMENT

For all the furnaces mentioned in this section, that is reduction retort furnaces, distillation retort furnaces, and muffle furnaces, air pollution control is achieved with a baghouse. In the above-mentioned installation for a muffle furnace, a low-efficiency cyclone and a baghouse are used to control the emissions from the sweating chambers and residue pouring operations of the three muffle furnaces. Although the cyclone has a low collection efficiency, it does collect from 5 to 10 percent of the dust load and it is still used. The cyclone was in existence before the baghouse was installed.

The baghouse is a six-section, pull-through type using 5,616 square feet of glass cloth filtering area. The filtering velocity is 3 fpm and the bags are cleaned automatically at regular intervals by shutting off one section, which allows the bags to collapse. No shaking is required, and the collected material merely drops into the hopper below the bags.

Another exhaust system with a cyclone and baghouse is used to collect the zinc oxide manufactured by the muffle furnaces. The system has three inlet hoods, one for each furnace, and each is arranged to collect the zinc vapors discharged from the orifice in the condenser. The ductwork is manifolded into a single duct entering the cyclone, and dampers are provided so that any one or any combination of the hoods can be used at one time. Since the exhausted gases and zinc oxide are heated by the combustion of zinc and by the sensible heat in the zinc, about 350 feet of additional ductwork is provided to allow the exhausted material to cool down to 180°F before entering the baghouse.

The cyclone collects about 20 percent of the solid materials in the exhaust gases, including all the heavier particles such as vitrified zinc oxide and solid zinc. The baghouse collects essentially all the remaining 80 percent of the solids.

The baghouse collector is actually two standard nine-section baghouses operating in parallel. In this unit, orlon bags with a total of 16,848 square feet of filtering area are used to filter the solids from the gases. A 50-hp fan provides 30,500 cfm ventilation--15,250 cfm for each furnace. The filtering velocity is 1.8 fpm. The bags are cleaned at regular intervals by shutting off one section and shaking the bags for a few seconds. A screw conveyor in the bottom of each hopper conveys the zinc oxide collected to a bagging machine.

This system provides excellent ventilation for the installation. None of the zinc oxide discharging from the condensers escapes collection by the hoods, and no visible emissions can be seen escaping from the baghouse.

Dust collectors for other zinc-melting and zinc-vaporizing furnaces are very similar to the ones already described. Glass bags have been found adequate when gas temperatures exceed the limits of cotton or orlon. Filtering velocities of 3 fpm are generally employed and have been found adequate.

LEAD REFINING

Control of the air pollution resulting from the secondary smelting and reclaiming of lead scrap may be conveniently considered according to the type of furnace employed. The reverberatory, blast, and pot furnaces are the three types most commonly used. In addition to refining lead, most of the secondary refineries also produce lead oxide by the Barton process.

Various grades of lead metal along with the oxides are produced by the lead industry. The grade of product desired determines the type of equipment selected for its manufacture. The most common grades of lead produced are soft, semisoft, and hard. By starting with one of these grades and using accepted refining and alloying techniques, any special grade of lead or lead alloy can be made.

Soft lead may be designated as corroding, chemical, acid copper, or common desilverized lead. These four types are high-purity leads. Their chemical requirements are presented in Table 85. These leads are the products of the pot furnace after a considerable amount of refining has been done.

Semisoft lead is the product of the reverberatory-type furnace and usually contains from 0.3 to 0.4 percent antimony and up to 0.05 percent copper.

Hard lead is made in the blast furnace. A typical composition for hard lead is 5 to 12 percent