CHAPTER 11.4

Vapor-Phase Extraction

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Vapor-phase extraction technologies exploit differences in the vapor pressures of various substances to separate the more volatile constituents from other condensed matter. Volatile species of interest enter the vapor phase and are transported from the furnace vessel, condensed downstream, and recovered as value-added products or process intermediates or, in other cases, rejected as impurities. Key process parameters such as temperature, pressure, furnace atmosphere (gas composition), and vessel residence time require precise control to maximize separation selectivity.

In the chemical process industries, vapor-phase extraction is employed as a means of separating organic species in fractional distillation operations; petroleum refining and spirits alcohol production are familiar examples. Vapor-transport processes are also used in the materials science and engineering field as a means of effecting materials synthesis, materials separation and purification, and coating substrate materials. In extractive metallurgy, vaporization techniques are employed in many primary and secondary metal-extraction processes as well as in certain refining processes. Historical examples of metal extraction include mercury and zinc from ores, concentrates, or scrap while examples of the elimination of deleterious constituents in metal refining operations include expulsion of undesirable volatile contaminants such as arsenic and antimony from refractory gold ores and base metal concentrates (Alcock 1976; Rosenqvist 1974). Other industrially significant vapor-transport applications include coal gasification, flame and plasma spray coating, and chemical vapor deposition (Hastie and Hager 1990).

FUNDAMENTALS

For a given vapor metallurgy application, the most important process parameters are temperature, pressure, the compositions of the applicable condensed and gas phases, and residence time of the condensed phase at temperature. Selection of the appropriate combination of process parameters depends on the physical and chemical characteristics of the target constituents as well as those of the other matrix components. Vapor-phase chemistry can be extraordinarily complex, replete with uncommon valence states and the evolution of multicomponent and/or polymeric gas species. Multicomponent condensed-phase solutions present unique challenges because they exhibit nonideal thermodynamic behavior and are possibly subject to undesired reactions or interactions between components.

The most obvious and certain way to vaporize a pure substance is simply to boil it, which requires processing at an elevated temperature such that the vapor pressure of the target substance equates to one atmosphere (or one bar, depending on the convention) at the substance's normal boiling point. However, it is not always practical or economical to boil a substance to effect vapor-phase transport. Fortunately, many substances are sufficiently volatile that vaporization can be effected at temperatures well below their normal boiling points. Water, for example, readily evaporates at temperatures well below its boiling point in arid, low-humidity regions.

The equilibrium vapor pressure of a pure element "i" in its standard state is established by the free-energy relationship in Equation 1, where ΔG° represents the standard Gibbs free energy of the vaporization reaction, R is the ideal gas constant, T is the temperature of interest (kelvin), and P_i represents the equilibrium vapor pressure (atm) of pure substance i. P° represents the standard pressure, which is typically 1 atm (or 1 bar); when the standard pressure value is unity, it is frequently omitted from thermodynamic calculations. Two of the more frequently used values of the gas constant are 8.314 J/mole-K and 1.987 cal/mole-K.

$$\Delta G^\circ = RT\ln P_i/P^\circ \qquad \textbf{(EQ 1)}$$

The Van't Hoff reaction isotherm, shown in Equation 2, expresses the relationship between the free energy of reaction and the equilibrium constant. This equation is especially useful for identifying the theoretical process conditions or "windows of operating parameters" necessary to vaporize a given substance.

$$\Delta G_R = \Delta G_R{}^\circ + RT\ln Q \qquad \textbf{(EQ 2)}$$

In this equation, ΔG_R represents the Gibbs free energy of the vaporization reaction, and Q represents the reaction activity quotient, which is expressed as the ratio of the partial pressure of substance (P_{Me}) as a vapor to the activity of the substance

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in a condensed phase (a_{Me}), as seen in Equation 3. The activity of a pure condensed substance in its standard state is unity.

$$Q = P_{Me}/a_{Me} \qquad \textbf{(EQ 3)}$$

The numerical value of the equilibrium constant, K, equates to the reaction quotient under equilibrium conditions. The Van't Hoff reaction isotherm equation is frequently presented in the form shown in the following equation:

$$\Delta G_R = RT\ln(Q/K) \qquad \textbf{(EQ 4)}$$

Equation 4 ranks among the most useful relationships in chemical thermodynamics because it enables one to establish whether a reaction is possible under a given set of process conditions or, alternatively, to precisely define the operating conditions that must be imposed on the system to achieve a process goal. When the values of Q and K are identical, the ΔG_R value is 0 and the system is at equilibrium. If the Q:K ratio is less than 1, then ΔG_R has a negative value, indicating that the reaction is spontaneous. Finally, if the Q:K ratio is greater than 1, ΔG_R has a positive value, indicating that the reaction is not possible and that the reverse reaction is favored.

To create the thermodynamic driving force required to vaporize a given substance, it is necessary to define and impose process conditions under which the value of the reaction activity quotient becomes and remains less than the value of the corresponding equilibrium constant or, in other words, create conditions wherein *the equilibrium vapor pressure of the specie of interest exceeds its partial pressure above the condensed phase*. Thus, at temperatures below the normal boiling point of a substance, it is sometimes possible to create and sustain the necessary thermodynamic driving force by minimizing the partial pressures of the vapor species in the furnace atmosphere. The partial pressure of the nascent gas species can be minimized in several ways: (1) by reducing the total system pressure and thereby reducing the partial pressure of the vapor species; (2) by introducing an inert diluent gas to lower the concentration of the nascent gas species; (3) by continuously purging the system to remove the vapors as they evolve; or (4) by some combination of methods 1, 2, and 3.

Vaporization reactions are exclusively endothermic, so increasing temperature will always increase the vapor pressure of a substance. However, practical limitations often dictate the maximum operating temperature of a system. Although exceptions exist, vapor-phase extraction is generally practiced on substances with boiling points less than 1,000°C (Moore 1981). Downstream, the vaporized substances are condensed by controlled cooling of the process gas stream. Care must be taken to avoid undesired back reactions with other gas-phase constituents and/or entrained particulate matter, particularly if the purity of the condensed substance is of concern. Particulate matter is frequently omitted by mechanical separation (e.g., cyclones, baghouses, and electrostatic precipitators) prior to cooling to the point of incipient condensation (i.e., the dew point). In certain applications, it may be necessary to modify and control the chemical composition of the gas phase to condense a pure element or a particular compound.

In many applications, the target element or compound does not exist discretely in the matrix. Rather, it is a component in a solid or liquid solution. In such cases, the activity of the target substance cannot be assumed to be unity. In an ideal solution, the activity of a solute is equal to its mole fraction at all concentrations. However, few of the non-gas-phase solutions encountered in metallurgical applications exhibit ideal behavior; very dilute solutions are the exception. In nonideal or "real" solutions, solute activity ($a_{\underline{i}}$) generally relates to its concentration and, as shown in Equation 5, is the product of the mole fraction of the solute (X_i) and a system-specific proportionality constant or activity coefficient that is designated by the symbol "γ_i":

$$a_{\underline{i}} = \gamma_i * X_i \qquad \textbf{(EQ 5)}$$

Activity coefficient values typically change as the solute concentration varies, except in the dilute solution region. The dilute solution region is regarded as the solute concentration range over which the tangent to the activity curve coincides with the activity curve, as shown for a generic system in Figure 1 (not drawn to scale). The tangent deviates from the activity curve as the solute concentration increases. When the tangent extends below the activity curve, as shown in Figure 1, the solute is said to exhibit positive deviation from Henry's law and negative deviation from Raoult's law, meaning that the attraction between solvent and solute atoms exceeds that between like atoms. Conversely, positive deviation from Raoult's law means that the solute atoms are repulsed by the solvent atoms so that their "escape tendency" increases, a favorable situation when vapor-phase extraction of the solute is desired. The Henrian standard states are convenient for thermodynamic computations that involve dilute solutions and are conveniently defined as either 1 at. % (atomic percent) or 1 wt % (weight percent) of the solute dissolved in solvent. The activity constant in the dilute solution region is termed the *Henry's law constant*, which is designated by the symbol "f_i" in the following equation:

$$h_i = f_i * C_i \qquad \textbf{(EQ 6)}$$

In Equation 6, h_i represents the Henrian activity and C_i represents concentration, which may be conveniently expressed in units of weight percent or atomic percent. If the standard state is selected within the extremely dilute solution region, then the Henrian activity coefficient for the solute specie (f_i) is one and the solute activity equals its concentration.

The solubility of certain impurity elements in metallic solutions is quite limited, and this statement holds particularly true for dissolved gases. Gases rapidly dissolve in high-temperature liquid metal melts, and these melts quickly approach equilibrium. For this reason, thermodynamic calculations are often highly effective for evaluating dilute solution behavior. When diatomic gases are involved, the concentration of dissolved gas varies according to the square root of the partial pressure (P_{P2}) of the gas above the melt. This relationship, commonly known as Sieverts' law, is expressed by the following equation:

$$h_{\underline{G}} = K * P_{G2}^{0.5} \qquad \textbf{(EQ 7)}$$

where G_2 is a diatomic gas, and $\underline{G}$ represents the concentration of G in the melt. For example, consider the dissolution of diatomic phosphorous gas in liquid silicon according to the reaction in Equation 8. The free-energy expression permits calculation of the Gibbs free energy of reaction ($\Delta G°_R$, J/mol) for the dissolution of diatomic phosphorous gas (Takahiro et al. 1996).

$$\tfrac{1}{2}P_{2(g)} = \underline{P}_{\text{in silicon}} \qquad \textbf{(EQ 8)}$$

$$\Delta G°_R = -139{,}000\ (\pm 2{,}000) + 43.4\ (\pm 10.1)\ T\ (\text{J/mol})$$

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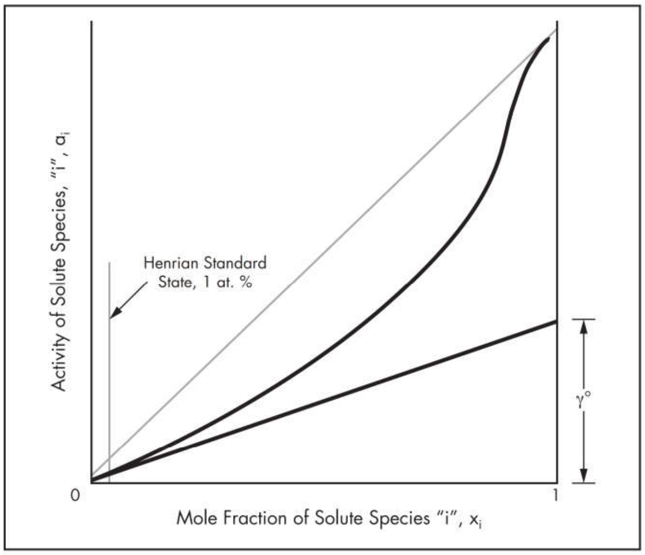

Figure 1 Activity of solute species "i" as a function of mole fraction

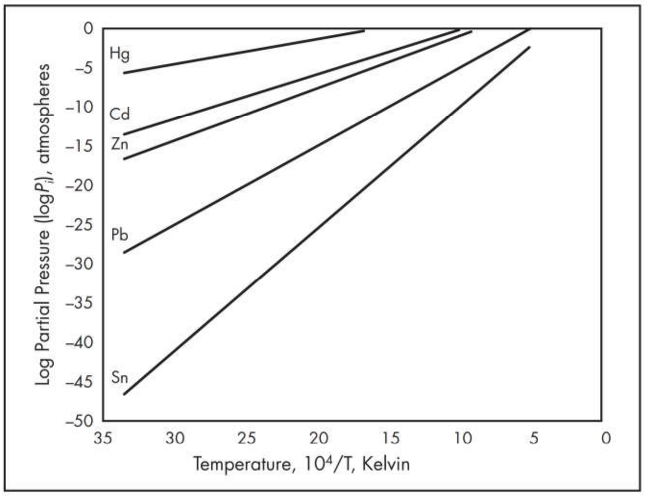

Figure 2 Van't Hoff diagram to illustrate the vapor pressures of five metals as a function of temperature (1 atm total pressure)

Experimental evidence that confirms Henry's law is valid for dissolved phosphorous concentrations up to 0.1%. The dissolution reaction in the following equation prevails for phosphorous concentrations less than 0.005% (Takahiro et al. 1996):

$$P_{(g)} = \underline{P}_{\text{in silicon}} \qquad \textbf{(EQ 9)}$$

$$\Delta G^\circ_R = -387{,}000\ (\pm 2{,}000) + 103\ (\pm 10)\ T\ \text{(J/mol)}$$

In either case, a numerical value for the equilibrium constant can be obtained from the appropriate free-energy equation. The equilibrium constant can then be written in terms of the dissolved phosphorous activity and the partial pressure of the phosphorous gas (P or P_2) above the melt. For the reaction involving diatomic phosphorous gas, the equilibrium constant will take the following form:

$$K = a_{\underline{P}}/P_2^{0.5} \qquad \textbf{(EQ 10)}$$

Presented in various formats, phase stability diagrams are used to define optimum process conditions. A Van't Hoff plot, such as the one shown in Figure 2, provides a simple example. These types of diagrams are constructed to illustrate the equilibrium vapor pressure of a specie of interest (expressed as the natural logarithm or base 10 logarithm) as a function of temperature (expressed as the reciprocal of temperature, K). The diagram can be used to identify temperatures at which complete vaporization is ensured (i.e., the temperature at which P_i exceeds atmospheric pressure). A second type of phase stability diagram is constructed to illustrate the stability regions of the condensed phases for the system in question. The axes of these two-dimensional isothermal diagrams typically represent two gaseous species that define the relevant potential of the atmosphere (e.g., carbon monoxide partial pressure versus carbon dioxide partial pressure can be used to define the oxygen potential of a system). Isobars that reflect the equilibrium vapor pressures of the relevant gas species can be superimposed atop the condensed phase fields. The diagrams are used to identify an "operating point" or a range of operating conditions that favor formation of the gas species. Kellogg presented a treatise on the construction, interpretation, and practical application of these diagrams (Kellogg 1966).

Another popular method for illustrating stable equilibrium phases are diagrams generated as a result of so-called free-energy minimization software, such as HSC Chemistry 9 (Outotec Technologies 2016). This software enables the user to define an initial composition and the temperature or pressure range (the other variable is held constant). Based on this input, the algorithm iteratively calculates the minimum free-energy curves and produces product plots of equilibrium composition versus temperature (or pressure).

Kinetic, mass transport, and heat transfer considerations can significantly influence behavior in vapor-phase extraction processes. Turkdogan et al. (1963) proposed a means to enhance diffusion-limited metal vaporization rates in metal/oxide systems. Diffusion-limited metal vaporization is complex and involves several system-specific and species-specific factors, the discussion of which falls outside the scope of this chapter. Subjectively, vapor pressures in excess of 0.1 atm typically result in rapid vaporization, 0.01 atm corresponds to slow vaporization, and 0.001 atm corresponds to a very slow vaporization rate (Kellogg 1966).

VAPORIZATION OF METALS

In general, the group 1 alkali metals and the group 2B metals, which include cadmium, mercury, and zinc, are quite volatile at relatively modest temperatures and are, therefore, excellent candidates for vapor-phase extraction. Conversely, the group 6A metals, which include chromium, molybdenum, and tungsten, exhibit characteristically low vapor pressures and are extremely poor candidates (Rosenqvist 1974). The vapor pressure of pure metals increases with increased temperature and follows an Arrhenius relationship, presented in general form in Equation 10, where A and B represent substance-specific constants and T is temperature (K).

$$\text{Log } P_i = A/T + B \qquad \textbf{(EQ 11)}$$

The simplest vapor-phase extraction operations involve direct vaporization of a single element. Although it is not exclusively the case, most metals evaporate as monatomic vapors. Mercury is a case in point:

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$$\mathrm{Hg_{(c)} \rightarrow Hg_{(g)}} \quad \textbf{(EQ 12)}$$

Because mercury is a noble metal that is relatively easy to produce, some of the earliest vapor-phase metal extraction applications involved mercury extraction and refining. Although mercury extraction can and has been done in a variety of furnace types and configurations, including rotary tube and multiple-hearth furnaces, mercury extraction is now commonly performed under vacuum in indirectly heated vessels called retorts. Retorts typically operate in the batch mode when processing scrap or, in environmental applications, a mercury-contaminated matrix such as sludge or soil. The mercury-bearing feed materials are sized and placed in trays before admission to the retort. The normal boiling point of mercury is 357°C, so it is advantageous to heat the charge above this relatively low temperature to maximize extraction. Mercury vaporizes, exits the retort, and is subsequently condensed and recovered downstream in chilled condensers and carbon filters. Process parameters may be controlled to dictate whether the mercury is recovered as metal for recycle or condensed as a specific compound in preparation for disposal. The U.S. Environmental Protection Agency (EPA 1990) lists retorting as the best demonstrated available technology under their land disposal restrictions.

While most metals tend to vaporize as monomers, many metalloids and compounds vaporize as polymeric species. For example, arsenic is a troublesome impurity that is often vaporized as part of a metal refining process such as copper and nickel converting and fire refining. Elemental arsenic vaporizes as a combination of As, $\mathrm{As_2}$, and $\mathrm{As_4}$ molecules.

VAPORIZATION OF COMPOUNDS

Vaporization is applied to a wide range of compounds, including carbides, nitrides, tellurides, halides, oxides, and sulfides of many common and exotic metals (Kellogg 1966). As with elemental mercury, most common mercury compounds are quite volatile and, therefore, amenable to vapor-phase extraction. In small-scale operations, mercury retorts process mercury-bearing materials in batch mode, whereas continuous rotary kilns or multiple-hearth furnaces are preferred for larger industrial operations. As high as 95% recovery as commercial-grade (99.9%) mercury is achieved through careful selection, application, and control of process conditions. Full or partial dissociation of a compound frequently leads to the formation of the metal vapor. Accordingly, mercury oxide decomposes when it is heated above 450°C according to the following reaction:

$$\mathrm{2HgO = 2Hg_{(g)} + O_{2(g)}} \quad \textbf{(EQ 13)}$$

This mode of behavior, dissociation leading to two separate gaseous species, is consistent with the behavior of several other metals compounds. In a second example, zinc sulfide (ZnS) dissociates to zinc and sulfur gases, as shown in Equation 14. Upon cooling, the reverse reaction occurs to condense zinc sulfide.

$$\mathrm{ZnS_{(s)} = Zn_{(g)} + 0.5S_{2(g)}} \quad \textbf{(EQ 14)}$$

Evaporation may occur due to partial dissociation, as is the gas with the dissociation of silica to form silicon monoxide gas and oxygen, as shown in the following equation:

$$\mathrm{SiO_{2(g)} = SiO_{(g)} + 0.5O_{2(g)}} \quad \textbf{(EQ 15)}$$

Some volatile compounds directly evaporate without dissociation. Arsenic trioxide ($\mathrm{As_2O_3}$) evaporates according to the following reaction:

$$\mathrm{2As_2O_{3(s)} \rightarrow As_4O_{6(g)}} \quad \textbf{(EQ 16)}$$

A metal that occurs in a compound may be vaporized by means of chemical reaction with a gas in a process generally known as “roasting.” Relatively nonvolatile metals can be extracted at temperatures far below their boiling points if gaseous compounds with suitable properties can be formed. For example, elemental mercury can be recovered from cinnabar (HgS), the most abundant mercury mineral, by roasting in an oxidizing atmosphere, as shown in the following equation:

$$\mathrm{HgS_{(s)} + O_{2(g)} = Hg_{(g)} + SO_{2(g)}} \quad \textbf{(EQ 17)}$$

Vapor metallurgical refining of nickel provides an interesting example of volatile compound formation in a refining application. Gaseous nickel tetracarbonyl ($\mathrm{Ni(CO)_4}$) forms when nickel and carbon monoxide react at relatively low temperatures (between 40° and 90°C) according to the reaction in Equation 18. The reverse reaction (nickel tetracarbonyl decomposition) occurs when the gas is heated into the 150°–300°C range (Boldt 1967). Thus, nickel can be selectively extracted by exposing the feed matrix (typically impure granules that contain pre-reduced nickel metal) to carbon monoxide to form the volatile nickel tetracarbonyl, which exits in the vessel discharge gases. The gas is filtered to remove entrained particulate, and then condensed downstream for recovery. In one industrial configuration, the nickel condensed on a circulating stream of nickel pellets and a bleed stream of the product pellets advanced to market.

$$\mathrm{Ni_{(s)} + 4CO_{(g)} = Ni(CO)_{4(g)}} \quad \textbf{(EQ 18)}$$

Polymeric compound families include oxides, sulfides, and chlorides, to name just a few.

TECHNOLOGIES

As with most other aspects of pyrometallurgy, no universally applicable vapor-phase extraction or refining technologies exist. Most industrial processes are highly commodity specific, because they have been developed to deal with the unique physical and chemical properties associated with a particular metal, its matrix (ore, concentrate, scrap), and its naturally occurring impurities. Vapor-phase extraction is performed using heated rotary calciners, rotary kilns, multiple-hearth furnaces, static-bed and fluidized-bed reactors, reverberatory furnaces, blast furnaces, electric arc furnaces, among other furnace types. Technological distinctions include the choice of indirect versus direct heating, batch versus semi-batch versus continuous processing, furnace atmosphere control and limitations, and cocurrent versus countercurrent gas-to-solids flow. Process gas handling system requirements must be decided on a case-specific basis. Some common equipment applied for capture and recovery of vapors include absorption towers/scrubbers, baghouses, and electrostatic precipitators. In this section, some of the more popular vapor-phase extraction vessels are summarily described.

Rotary tube furnaces are applied to a very wide variety of thermal processing applications that include drying, calcination, pyrolysis, roasting, thermal desorption (selective removal of volatile contaminants), thermal oxidation, and vitrification. Rotary tube furnaces are amenable to many

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vapor-phase extraction applications. A rotary tube furnace is a cylindrical reactor that rotates about its longitudinal axis. The tube is usually inclined to the horizontal. Commercial reactors are typically 0.3–3.6 m diameter and the length-to-diameter ratio generally ranges from 4 to greater than 10. In some applications, sections with expanded diameter are included to increase burden depth and residence time. The tube ends are sealed by various means to prevent gas leakage, and maintaining slight negative pressure (0.02–0.20 mm of mercury) in the furnace also helps control emissions. Draft is provided by exhaust blowers and gas fans that are typically located downstream of the furnace. Ideal feed materials are granular, free-flowing solids that do not soften, agglomerate, or melt at the process temperature. Feed enters the higher end of the cylinder and works its way through the cylinder because of head (feed rate), rotational speed (rpm), and slope. These factors dictate the residence time of the burden in the tube. Finished product discharges at the lower end of the tube.

Rotary tube furnaces can operate in batch, semicontinuous, or continuous mode. Process gases may flow in the same direction (cocurrent) or in the direction opposite (countercurrent) to the solids through the rotary tube. The gas flow rate and direction affects solids residence time in the tube. In applications that involve chemical reactions between constituents in the gas and condensed phases, kinetic implications are associated with each configuration, with countercurrent gas versus solids flow providing advantages with respect to reactant concentration at both ends of the tube. Countercurrent gas-to-solids flow also improves heat transfer efficiency. Cocurrent flow is used to dry heat-sensitive materials at higher inlet gas temperature because of rapid gas cooling during the initial evaporation of surface moisture.

Rotary tube furnaces may also be classified as directly or indirectly heated, although hybrid units exist. *Directly heated* or "direct heat" means that the solid charge is heated by combustion or preheated gases that pass directly over the surfaces of the charge solids. Directly heated rotary kilns are among the most important industrial furnaces used for continuously conducting relatively high-temperature operations. In a directly heated rotary kiln, the interior surface of the metal tube (shell) is lined with insulating block and/or refractory brick. Lengths in excess of 50 m are common. Diameters may be constant or vary along the length of the kiln; some kilns have an expanded diameter to increase residence time in a particular heating zone.

Directly heated units are usually more economical to operate but are generally unsuited for applications that require close furnace atmosphere control. In some situations, diluting the process gas with combustion gas may be desirable. Gas volumes and velocities are relatively high (~30 m/min) in direct-fired units because the heat is transferred from combustion gas to the solid charge. The high gas velocity causes fine solid particles to be entrained in the cylinder discharge gas, which requires downstream dust capture-and-control measures.

Indirectly heated means that the heating medium does not directly contact the solid charge. Indirectly heated rotary calciners are metal cylinders surrounded by stationary, refractory-lined gas-fired or electrically heated furnaces or "fireboxes." Indirectly heated calciners require a minimum purge gas flow through the cylinder and are well suited for gas-sealed operation under controlled oxidizing, reducing, or inert atmospheres with minimal dusting. The temperature that these units can sustain mainly depends on the cylinder material: carbon steel is satisfactory for maximum temperatures between 375° and 425°C; stainless steel is satisfactory for 540°–760°C; Inconel and other alloys can sustain higher temperatures; and graphite is reserved for extremely high temperatures (>2,000°C). Lifters may be longitudinally positioned on the inner tube surface to prevent charge material from sliding. Thermal efficiency can range from 40% to 70%.

Multiple-hearth (sometimes termed "multi-hearth") furnaces are vertical steel towers that contain a series of circular refractory hearths. The feed material is introduced in the top hearth and progresses downward through a series of hearths. The center shaft slowly rotates rabble arms on each hearth to turn over the charge and push it across the hearth to drop holes, which are located near the outside of one hearth and near the center shaft on the next hearth. Gases typically flow upward and countercurrent to the charge for improved mass and heat transfer.

Suspension roasting is essentially a modification of multiple-hearth roasting wherein feed is dried and preheated on the upper hearths and then falls through the center section of the furnace, countercurrent to the upwardly flowing oxidizing furnace gas. Flash or autogeneous roasting is a variation of this theme; preheated ore is injected along with preheated air. The process is effective with sulfide minerals that oxidize exothermally and require little or no supplemental fuel. However, the benefits of countercurrent operation are sacrificed.

Fluidized-bed roasting is attractive because very large mass and heat transfer coefficients exist between solid and gas. Gases pass upward through a solid (0.02 to 2 mm in diameter) particle bed. At low gas flow rates, the gas permeates the bed without moving the particles, and the pressure drop across the bed is proportional to gas flow rate. As gas velocity approaches a critical value, the bed expands as the effective particle masses are balanced by the drag forces imposed by the gas stream. Over a narrow range of velocities, the particles become individually suspended with a downward velocity relative to the gas stream approximately equal to its terminal velocity. Bed expansion occurs as gas velocity continues to rise, so the distance between particles increases and the pressure drop across the bed diminishes. At even higher gas velocities, bed expansion ceases and the pressure drop is independent of gas velocity. The bed assumes fluid characteristics and its appearance resembles that of a boiling liquid with bubbles rising through the bed and bursting at the surface. Within this state of aggregative fluidization, loose particle clusters (dense phase) are dispersed in a gas atmosphere that contains individual particles (lean phase). Gas-to-solid contact is exceptionally high because of the turbulent bed conditions while the relative velocity between gas and solid particles is within the laminar flow range. Heat transfer and mass transfer rates are very high in fluidized beds. Effective thermal conductivities of fluidized beds have been measured to exceed about 100 times that of silver. Convective heat transfer ensures uniform bed temperatures.

APPLICATIONS AND UNIT OPERATIONS

Numerous examples of historical and current industrial implementation of vapor-phase extraction technologies are available. The following discussion is not intended to be comprehensive. It offers specific examples that have commercial precedents and, in most instances, reflect prevailing industrial practices.

Drying is unquestionably the most frequently practiced industrial vapor-phase extraction process. In many

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applications, a substantial portion of the bulk water content is removed by sedimentation, filtration, centrifugation, or other mechanical means. However, the processed material invariably retains a considerable moisture content. Drying is typically the preferred alternative when circumstances demand a low to negligible free-moisture content. In general, drying is an evaporative process that is conducted at relatively low temperatures (typically 90°–200°C). On the industrial scale, drying is performed in many equipment types, and equipment selection depends on factors such as the physical and chemical characteristics of the material to be dried, the physical and chemical characteristics of the liquid phase, and the initial and final moisture contents. Because drying operations generally do not require tight furnace atmosphere control, directly heated fossil-fuel-fired rotary tube furnaces are frequently the technology of choice.

Selective vaporization and distillation exploits differences in vapor pressure to separate components in a solution. When a significant vapor pressure difference exists between two or more components in a solution, the components can be separated by selective volatilization of the component with the greater vapor pressure. As the matrix is heated to an appropriate temperature, the vapor phase becomes enriched with the more volatile component as the liquid phase is depleted of the same. Classically, selective volatilization and distillation is performed in batch and continuous (or fractionating) reflux columns with preference for continuous systems in high-throughput operations. In such systems, the liquid is introduced near the center of a tall vertical column. Within the column, a series of trays is positioned to allow liquid to cascade from one tray to the next while gas rises from upward through series. Temperature in the lower portion of the column is maintained below the boiling point of the less volatile constituent and above the boiling point of the more volatile constituent. The temperature in the upper portion of the column must also be low enough to permit the less volatile element to condense. Consequently, the less volatile element accumulates and is removed from the bottom of the column (i.e., "bottoms") while the more volatile element exits the column as vapor and is condensed and recovered downstream.

Cadmium and zinc have normal boiling points of 765° and 905°C, respectively. Thus, cadmium can be selectively separated from zinc by virtue of its greater volatility. Magnesium–lead alloy is an example of a metallurgical azeotropic system. Simple distillation is incapable of separating the two components in a binary azeotropic mixture, wherein an intermediate compound vaporizes instead of an individual component. In this example, liquid Mg_2Pb vaporizes without change in composition; this behavior is analogous to a congruent melting point in a condensed phase system. Azeotropic behavior can sometimes be managed by altering the system pressure or by adding another component that has a strong affinity for one of the original components.

On occasion, it is desired to remove a metal or compound that does not exhibit a sufficiently substantial vapor pressure at elevated temperature. Under such circumstances, it may be expedient to instigate a chemical reaction to form a volatile compound that is better suited for vapor-phase extraction. In extractive metallurgy, the term *roasting* applies to a wide variety of thermal processes that are typically performed as a pretreatment process to render some component(s) in the feed material amenable to subsequent processing in a separate unit operation. Roasting is performed for the specific purpose of causing a chemical change in one or more selected feed components. It is usually performed at elevated temperatures that do not cause an appreciable degree of charge fusion or sintering, as these phenomena are usually detrimental to the process objective. Ideally, the roaster product, termed *calcine*, is a free-flowing, loosely agglomerated powder. Roasting processes are classified in many ways, often according to objectives such as oxidizing, reducing, chloridizing, sulfatizing, or magnetizing. In some instances, the sole purpose of the roasting step may be to eliminate an undesired volatile species such as arsenic. Once in the gas phase, these materials exit the reactor in the discharge gas stream and condense downstream as the gas cools.

Carbothermic reduction and vaporization was once the primary method for zinc extraction and refining. Zinc vapors were produced by processing zinc concentrates in horizontal and vertical retorts. The condensate was refined in similar manner to achieve the specified grade. This technology is considered obsolete, having been supplanted by the roast-leach-electrowinning processes. However, vapor metallurgy processes are currently used in the secondary industries to extract zinc from primary smelting slags (slag fuming) and from electric arc furnace (EAF) dust.

Slags produced in primary nonferrous smelting operations often contain appreciable concentrations of volatile and potentially valuable constituents such as lead, zinc, and/or tin. Slag fuming operations are generally performed in a separate, dedicated batch furnace where the zinc-bearing feed material and reductant (e.g., metallurgical coke or fine pulverized coal) are injected into molten slag. The slag is blown with air to create a strongly reducing environment conducive to carbothermal reduction of zinc via contact with the solid reductant or, more probably, the carbon monoxide that forms via the Boudouard reaction, which is shown in Equation 19. Lead, zinc, or tin are reduced to their respective metals and then vaporize and exit with the furnace discharge gas. The metals reoxidize and form fine particulate matter upon cooling and are recovered for further processing to produce metal or marketable compounds. Slag fuming is characterized by high process temperatures (~1,300°C), low oxygen potential, and good bath mixing.

$$C_{(s)} + CO_{2(g)} = 2CO_{(g)} \tag{EQ 19}$$

EAF dust contains relatively high concentrations of zinc that come from galvanized scrap in the EAF charge. The Waelz kiln process has emerged as the predominant method for recycling zinc contained in EAF dust. The contained zinc is present as franklinite (ZnO) and zinc ferrite ($ZnFe_2O_4$). To effect the zinc reduction and vaporization, a pelletized mixture of EAF dust, a carbonaceous reducing agent (coke), and slag formers (sand and lime) are charged to the rotary kiln. Typical kiln dimensions are 50 m long by 3.6 m in diameter. The kiln operates with countercurrent gas-to-solids flow and provides 4–6 hours of reaction time. The zinc is removed by roasting the dust in the presence of the carbonaceous reductant according to the reactions shown as Equations 20 and 21. Iron and the other nonvolatile EAF dust constituents form an iron-rich slag phase.

$$ZnO_{(s)} + C_{(s)} = Zn_{(g)} + CO_{(g)} \tag{EQ 20}$$

$$ZnFe_2O_{4(s)} + 4C_{(s)} = Zn_{(g)} + 2Fe_{(s)} + 4CO_{(g)} \tag{EQ 21}$$

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Once the zinc vapor enters the kiln atmosphere, it is oxidized by the oxygen in the combustion gas, as indicated by the following reaction:

$$Zn_{(g)} + ½O_{2(g)} = ZnO_{(s)} \qquad \textbf{(EQ 22)}$$

Other volatile constituents, such as lead and cadmium, enter the vapor phase during carbothermal reduction and are reoxidized in the furnace atmosphere. The crude Waelz oxide assays 60%–65% zinc and contains impurities that include cadmium oxide and lead oxide. The oxides may be subject to further thermal or hydrometallurgical processing to produce marketable zinc oxide or zinc metal (Mager and Meurer 2000).

In extractive metallurgy, volatile gaseous halides figure prominently in transporting material from one solid to another. Most metal halides are volatile or have relatively low decomposition temperatures, which makes volatilization appear to be an expedient way to separate certain refractory metals, provided that it is possible to exercise adequate control of the halide potential. Halide stability decreases in the following order: iodide, bromide, chloride, fluoride.

A commonly effective treatment scheme involves performing a chloridizing roast to convert certain target metals to their volatile chlorides and a subsequent or simultaneous volatilizing roast. The pressure range of interest for establishing the behavior of volatile metal chlorides ranges from 10^{-10} to 1 atm. Volatile metal compounds, particularly chlorides, are extracted by vapor-transport processes, purified by fractional distillation, and reduced to metal. Titanium production is an example of chlorination roasting applied to abet vapor-phase transport, but the process is also applied in the production of hafnium, niobium, uranium, and zirconium (among other metals).

Titanium oxide (TiO_2) in the form of natural or synthetic rutile is converted to titanium tetrachloride ($TiCl_4$) in static- or fluidized-bed chlorinators. A static-bed chlorinator accepts feed in the form of briquettes made of rutile and a carbonaceous reductant such as metallurgical coke, while a fluidized-bed chlorinator is fed with rutile and ground coke. In both cases, chlorine (Cl_2) gas is injected at the bottom of the chlorinator and flows upward through the bed that is heated to between 800° and 1,000°C by the enthalpy of the exothermic reaction supplemented by electrical resistance (carbon electrodes) heating. Titanium tetrachloride gas forms according to the following carbochlorination reaction:

$$2TiO_2 + 3C + 4Cl_{2(g)} = 2TiCl_{4(g)} + 2CO_{(g)} + CO_{2(g)} \qquad \textbf{(EQ 23)}$$

The reaction requires excess chlorine because chlorine efficiency is between 75% and 85%. The carbon tetrachloride exits with the chlorinator discharge gas stream that also includes carbon dioxide, carbon monoxide, unreacted chlorine, and entrained particulate matter. Following coarse particulate removal in a cyclone, the chlorinator discharge gas enters a direct-contact cooling tower. A circulating stream of liquid titanium tetrachloride is sprayed into the freeboard to reduce gas temperature and condense titanium tetrachloride liquid, which collects at the bottom of the tower. Following separation from sludge and other insoluble matter, the crude titanium tetrachloride contains iron, vanadium, silicon, tin, and other metallic impurities that were also converted to chlorides. Most of these chlorides are insoluble in titanium chloride and are readily separated by fractional distillation. Vanadium oxychloride ($VOCl_3$) is an exception that requires chemical precipitation for removal. The resulting titanium tetrachloride is approximately 99.8% pure and is stored under inert gas, pending further processing to produce titanium oxide pigment or titanium sponge via the Kroll process or the Hunter process (Gill 1980).

Magnesium production via the Pidgeon process involves a silicothermic reduction process that is performed in nickel-chromium steel retorts. The retort charge consists of a 5:1 ratio of calcined dolomite and ferrosilicon (FeSi) that has been ground, mixed, briquetted, and preheated to approximately 700°C (Gill 1980). Inside the retort, silicothermic magnesium reduction proceeds according to the following reaction:

$$MgO \cdot CaO_{(s)} + FeSi_{(s)} = 2CaO \cdot FeSiO_{2(l)} + 2Mg_{(g)} \qquad \textbf{(EQ 24)}$$

The cylindrical retorts are horizontally oriented in a fossil-fuel-fired furnace such that one end of the retort extends outside of the furnace. While the heated zone of the retort is maintained at approximately 1,150°C, a vacuum connection draws the nascent magnesium vapor into the water-cooled extension, where magnesium crystals condense on a removable steel sleeve. At the end of the retorting cycle, the resulting 99.98% magnesium ring or “crown” is withdrawn, melted, and cast. Calcined dolomite (dolime) is the preferred feed material (versus magnesium oxide) because the calcium oxide in the dolime improves magnesium yield by displacing magnesium oxide taken up in the dicalcium silicate slag (Gill 1980).

Vapor-phase transport is extensively employed in modern steelmaking operations to expel dissolved impurities such as hydrogen and nitrogen, which exist in their atomic forms in liquid steel. Unless the concentrations are reduced, these impurities generally cause deleterious effects on the steel product characteristics. Multiple variations on the theme have been practiced, but, in essence, a ladle that contains a charge of molten metal to be refined is placed within a chamber where the total pressure can be lowered to minimize the partial pressure of the target gaseous impurity above the melt. Commercial vacuum systems operate at pressures as low as 0.1 torr.

Vapor-phase removal of hydrogen and oxygen take place in accordance with Sieverts’ law, which states that the dissolved gas concentration is proportional to the square root of the partial pressure of the gas above the melt. The relevant reactions are expressed as Equations 25 and 26. Modern degassing operations are also effective in decarburizing molten steel because the vacuum promotes reaction between carbon and oxygen to produce carbon monoxide gas, as indicated by the reaction in Equation 27.

$$\underline{H} = ½H_{2(g)} \qquad \textbf{(EQ 25)}$$

$$\underline{N} = ½N_{2(g)} \qquad \textbf{(EQ 26)}$$

$$\underline{C} + \underline{O} = CO_{(g)} \qquad \textbf{(EQ 27)}$$

Vacuum degassing of steel is often performed by situating the ladle bearing the molten steel near a vacuum chamber such that snorkels can extend from the chamber into the melt. Steel is degassed at nominal temperature and total pressure of 1,600°C and 1 torr, respectively (Ghost 2001).

Vacuum refining is also applied in nonferrous metal refining operations. Refining lead bullion produced via primary or secondary smelting operations entails a series of batch operations that are typically conducted in large steel kettles. In the usual sequence, these operations include drossing (copper

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removal), softening (antimony and arsenic removal), desilverizing, dezincing, and debismuthizing. Dezincing is generally accomplished by vacuum refining. A kettle fitted with a bell-shaped vacuum lid is charged with desilverized lead. Vacuum is applied as the molten lead is heated to, and maintained at, approximately 600°C. Over several hours, dissolved zinc is drawn into the vapor phase and subsequently condenses on the inner surface of the bell. The zinc returns to the desilverizing process (Parkes process), where it is used to remove precious metals, mostly silver, from the lead.

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