METALLURGICAL USES

FLUXES FOR METALLURGY

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A metallurgical *flux* is a substance that is added to combine with gangue (unwanted minerals) during ore smelting, with impurities in a molten metal, or with other additives in metal refining processes to form a *slag* that can be separated from the metal. Because slags are immiscible with the metallic melt and are of lower density, a separation of the slag and metal occurs if the viscosity and surface tension are of the proper values. The chemistries of slags are adjusted to provide the proper melting point, viscosity, surface tension, conductivity, specific heat, density, or chemical properties to effect the desired task. In addition to absorbing impurities from the metal, the purposes of the slag are to thermally insulate the metal bath, protect the molten metal from the atmosphere, and control the chemical potential of the system. Several excellent references on slags and metallurgical fluxes are available (Boynton, 1980, Lankford, Jr., et al., 1985, Turkdogan, 1983, Rosenqvist, 1974, Fine and Gaskell, 1984).

The function of the slag might vary at different stages within a process prior to final melting. For example, the slag composition and behavior will change as materials descend in the iron blast furnace, or as they melt in the early stages of formation of steelmaking slags. Selection of the chemistry for a slag might be influenced by factors outside the primary function as when blast furnace slags are used to make cement, rock wool insulation, or fertilizer supplements. Sometimes slags contain a sufficient amount of valuable recoverable elements to be sold as raw materials for other processes.

Fluxes are often referred to as *acid, basic,* or *neutral.* Acid fluxes are those that generally form acids in water and bases are those that would generally form bases in water. Typical acid fluxes are silica, alumina, and phosphorus, although alumina can function as either an acid or base. Typical basic fluxes are lime and magnesia. Fluorspar, or calcium fluoride, is a neutral substance because it can be viewed as the reaction product of a base and an acid. The degree of acidity (ratio of acids to bases) or basicity (ratio of bases to acids) is often specified to characterize the slag chemistry for a particular system. The system might also be referred to as acid or basic depending on the choice of slag, for example, basic steelmaking uses slags with more bases (lime and magnesia) than acids (silica and alumina).

Many forms of minerals and compounds have been used as fluxes depending on the process requirements, availability, costs, requirements for recycling of intermediate products, and environmental concerns. Because slags are most often mixtures of oxides and silicates, fluxes are usually oxides, carbonates (which decompose to oxides) and silicates. Slags comprising phosphates, borates, sulfides, carbides, or halides have also been used (Rosenqvist, 1974, Moore, 1981, Szekely et al., 1989). In ironmaking and steelmaking, slags are basic, and the primary flux added is lime-bearing, although some acidic components are sometimes added. In nonferrous processes slags and fluxes are acidic with silica as the primary component, and although the use of basic flux such as limestone or lime is not extensive, some amount is used to modify slag properties and some refining slags are lime based.

The production of iron is accomplished by smelting of ores, pellets, and sinter in blast furnaces with subsequent refining of molten iron and scrap in oxygen-blown processes. The electric furnace is used to make steel, stainless steels, ferroalloys, and special alloys, whereas ferromanganese is often made in blast furnaces. Fluxes are used in all of these processes, and either limestone or lime is the major flux component with some dolomite, dolomitic lime, silica, alumina, and fluorspar being used. In ironmaking, the flux is added either by direct charging or through sinter and fluxed pellets. In steel refining by the basic oxygen process, flux is added as lime and dolomitic lime that are either charged as lumps or injected as fines. Some small amount of limestone is sometimes used. Fluorspar is often added as lumps or mixed with other fine materials in briquettes. Alumina is sometimes added to blast furnaces either by direct charging of sized lumps or through sinter.

Typical acid fluxes are sand, gravel, quartz rock, used silica brick, or raw siliceous ore (Lankford, Jr., et al., 1985). Olivine, which is a magnesium-silicate mineral, has been added to iron blast furnaces to enhance removal of alkalis (Lankford, Jr., et al., 1985). Alumina in the form of bauxite, aluminiferous clay, and recycled alumina brick has been used as flux. Alumina can function amphoterically as either an acid or base, for example it can form aluminum silicate in high silica slags or calcium aluminate in lime-bearing slags (Lankford, Jr., et al., 1985).

Limestone (calcium carbonate) and dolomite (magnesium-calcium carbonate), or fluxstones as they are sometimes called (Boynton, 1980), and their calcined forms, lime and dolomitic lime are the major basic fluxes. In the latter cases, the carbonates are decomposed in a kiln-type process to drive off carbon dioxide that might otherwise interfere with the subsequent smelting or refining process or require expensive forms of energy to effect the decomposition (e.g., by combustion of coke in the iron blast furnace). Limestone is considerably less expensive than lime because it is not calcined; however, lime is far more difficult to handle and reacts readily with water. Dolomite and dolomitic lime are used for their magnesia content.

Fluorspar is a neutral flux often used as an additive in steelmaking slags to improve fluidity, but it has also been used in combination with lime as a primary slag in electroslag refining (Duckworth and Hoyle, 1969). Fluorspar is available in several grades, with the lowest grade often used for steelmaking. When the price of fluorspar has risen, substitutes including aluminum smelting dross, borax, manganese ore, titania, iron oxides, silica sand, and

calcium chloride have been used (Peters, 1982). Briquettes containing various combinations of low grade manganese ore fines, mill scale, precipitator dust, recycled slag, and fine fluorspar have been used as an addition to the steelmaking process to form a fluid slag.

Some flux materials are added to repair smelting and refining vessel refractory linings. The selection of the flux to be added depends on the type of process and type of refractory. In the basic oxygen process for steel, lime from the flux combines with silica formed by oxidation of silicon from the metal to form a slag. The steelmaking vessel is lined with basic magnesia brick that will be attacked by the slag, so common practice includes addition of 5 to 10% magnesia (magnesium oxide) to help prevent attack on the refractory in the vessel (Boynton, 1980, Lankford, Jr., et al., 1985). In copper smelting, an acid slag practice is used, and silica is added for repair of refractories in some parts of the smelting furnaces (Anderson, 1961, Fowler, 1961).

The slag formed in one operation can also serve as a flux in another. Slags formed in refining operations are often recycled to a smelting operation to provide valuable flux materials and also to recover elements that otherwise might be lost. For example, steelmaking slags are recycled to the blast furnace smelter to recover unreacted, pre-calcined lime, iron, and manganese oxides. The limitation on the recycle of steelmaking slag to the iron blast furnace is typically the impurity content, particularly the sulfur, phosphorus, and zinc. In copper smelting, converter slags can be recycled to recover copper and flux. The amount recycled is affected by the minor elements such as bismuth, antimony, and arsenic.

Since about 1980, ironmakers and steelmakers have been using synthetic slags for external treatment of hot metal from the blast furnaces and for treatment of steels in ladles subsequent to basic oxygen and electric furnace processing. These treatments include reagent additions for removal of silicon, sulfur, and phosphorus. There have been applications in nonferrous metallurgy, the ferroalloy industries, and foundries as well (Szekely et al., 1989). Synthetic slags are made through additions of magnesium or aluminum metal, magnesium-aluminum or calcium-silicon alloys, calcium carbide, prefused calcium aluminate, and mixtures of some of the above with coke, lime, and fluorspar (Stubbles, 1984). Sodium carbonate (soda ash) can be used for desulfurization and dephosphorization of steel (Szekely et al., 1989, Yamamoto et al., 1980). Special synthetic compounds are also used as mold fluxes in the continuous casting of steel (Branion, 1987).

INDUSTRY STRUCTURE

About 90% of all metal consumed in the United States and in the world is iron and steel (Anon., 1991a, Habashi, 1986), and consequently, use of flux is preponderantly in the iron and steel industry. In the United States, metallurgical flux required by both the ferrous and nonferrous industries is abundant, and most of the demand is satisfied by domestic production with the exceptions of fluorspar and alumina. Fortunately, the major flux minerals limestone, dolomite, and silica are widespread throughout the world, although there are examples where an adequate flux source was not available and this affected the process selection.

Limestone and Dolomite

Limestone and dolomite fluxes used for ironmaking and steelmaking in the United States originate primarily from Michigan. Historically, these fluxstones were found to be of the type and purity useful for ironmaking and could be readily and economically transported to iron and steel producing centers by lake boats and rail. Fluxstone is moved by barge where feasible. Fluxstone is also obtained in Ohio, Pennsylvania, and Illinois (Lankford, Jr., et al., 1985, Lawrence, Jr., 1975). Until recently, major iron and steel

producers owned limestone and dolomite quarries, but most have sold the operations and now recycle slags or purchase flux as needed.

Because limestone is very readily available around the world, a suitable source can almost always be found. Long distance transportation of stone is not common due to the low value and widespread occurrence. However, higher valued lime might be transported greater distances. In some special cases, due to the purity required, flux might be moved long distances. For example, low impurity flux has been transported from Japan to Australia to supplement local sources for use in fluxed pellets (Murray, 1988, personal communication).

For many years in the United States, limestone and dolomite were transported to the steel producing centers for use in blast furnaces, lime plants, and sinter plants. The sinter plants were often located at or near steel mills to take advantage of the availability of a variety of iron-bearing raw materials, coke fines, and slag. Recently, some major iron producers have incorporated flux into pellets, and the fluxed pellets are transported to iron producing centers.

The trend towards the use of fluxed pellets in blast furnaces has required a change in the transportation and distribution patterns of limestone and dolomite. In the United States, fluxed pellets are not made near the steel mills, but instead are made at the mines in Minnesota and Michigan that are located farther from the steel mills than the limestone and dolomite quarries. Therefore, the limestone and dolomite must first be transported to the mines before being returned to the steel mills in the form of fluxed pellets. Fluxed pellets made in Minnesota with flux from Michigan are transported as far as Alabama and Utah.

Extensive processing of limestone and dolomite materials is generally avoided; however, the economical production of materials for flux in the sizes desired by the customers requires that producers make a wide range of products for multiple markets. Thus, the limestone and dolomite in various sizes might also be sold for land erosion control, construction, aggregate, and agricultural purposes as well as for flux. The beneficiation process generally comprises only crushing, sizing, and washing. The sizes of stone used for flux are generally less than 15 cm but greater than 150 mesh (0.104 mm). The coarsest sizes are used for direct charging to furnaces, and intermediate sizes are used for lime burning, production of flux for fluxed pellets, and for sinter production. The finest sizes, often contain impurities and are disposed of as waste.

In the manufacture of fluxed pellets, the flux stone is crushed and ground to 60 to 80% passing 200 mesh (0.074 mm) thus with appropriate facilities for crushing, grinding, and sizing, there is some flexibility in the stone sizes that can be used. In fluxed pellets, a specific chemistry is usually targeted in terms of both lime and magnesia in relation to silica, and this requires a blend of limestone and dolomite. In some instances, the blend can be made from quarries in close proximity to one another, and this is the most economical choice. In other cases, the blend must be made with stones from separate locations, and blending is done while loading boats or at a blending site.

The US Bureau of Mines (USBM) publishes information on the production and consumption of crushed stone which includes flux (Tepordei, 1991). A directory of principal producers of crushed stone is also published annually (Anon., 1990). The major sources of limestone and dolomite in the United States are domestic, and the quantity used in the iron and steel industry is about 1% or less of total crushed stone consumption (Anon., 1987, Tepordei, 1991). The trend in the production and consumption of limestone and dolomite in the iron and steel industry is reported as Crushed Stone by the USBM as shown in Table 1. During the period 1975 to 1985, the amount of limestone and dolomite used by the iron and steel industry was reduced from about 22 to 9 Mt. During the same period, the value of stone increased from about $2.20 to $4.46/t, but

Table 1. Demand (Mt) and Prices ($/t) for Crushed Stone, Lime, and Fluorspar in Iron and Steel Production, 1975–1985

	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985
				a. Crushed Stone (Limestone and Dolomite)							
Demand	22	22	21	22	20	15	14	NA	8	NA	9
Total US	817	816	865	952	998	892	792	717E	782R	868E	909
Avg. Price, $/t[a]	2.20	2.47	2.59	2.73	2.91	3.30	3.66	3.95	4.27	4.33	4.46
1985 Price, $/t[b]	4.64	4.57	4.52	4.51	4.67	4.76	4.68	4.54	4.59	4.47	4.46
				b. Lime (Calcined Limestone and Dolomite)							
Demand	7.0	7.9	7.6	8.2	8.2	6.5	7.2	4.4	4.9	5.1	4.9
Total US	17.4	18.4	18.1	18.6	19.0	17.3	17.1	12.8	13.5	14.5	14.2
Avg. Price, $/t[a]	30.26	33.27	36.92	40.51	45.47	49.04	51.80	54.52	56.31	56.33	56.96
1985 Price, $/t[b]	56.28	58.88	61.23	62.70	64.59	63.94	61.52	60.91	60.62	58.20	56.96
				c. Fluorspar (Demand in Crude Steel Production Only)							
Demand	0.47	0.55	0.49	0.51	0.47	0.32	0.33	0.18	0.16	0.17	0.12
Total U.S.	1.13	1.15	1.05	1.09	1.03	0.89	0.84	0.48	0.51	0.68	0.52
Avg. Price, $/t[a]	86	95	106	112	122	150	176	191	181	W	NA
1985 Price, $/t[b]	162	168	175	174	174	195	209	213	195	W	NA

Adapted from USBM (Anon., 1987), NA = not available E = estimated R = revised W = withheld to avoid disclosing company proprietary data.
[a]Average annual price—FOB quarry, actual dollars/t.
[b]Average annual price—FOB quarry, based on constant 1985 dollars.

was about $4.40/t in constant 1985 dollars. From 1985 to 1989, the consumption of limestone and dolomite in the steel industry decreased further. In 1989, the consumption of limestone for flux was on the order of 4.3 Mt, and the consumption of dolomite was about 0.64 Mt (Table 2).

Lime

Lime and dolomitic lime produced by calcination of limestone and dolomite are widely used as fluxes in steelmaking. Some steel producers operate lime plants, and others purchase lime. Lime plants are sometimes located near steel consuming operations, and in some cases are connected by conveyor belts to the steel shops. In other situations, lime is transported by truck, barge, or rail. The sizes of stone required for lime burning are fairly well fixed and must be integrated with the needs of the entire steel operation when the limestone and dolomite operations are captive. Some nonferrous operations have operated captive lime plants, but in the nonferrous industries lime has uses in addition to smelting and refining such as treatment of acid wastes and control of acidity in flotation plants. The USBM has published a directory of lime plants in the United States (Anon., 1991b).

The USBM publishes data related to production and consumption of lime (Ober, 1989, Miller, 1990). Most lime is domestically produced, and about one-third of total lime demand arises from the iron and steel industry. The trends for the period 1975 to 1985 are shown in Table 1 and for 1986 to 1989 in Table 3. Consumption of lime for iron and steel use decreased by about 50% between 1975 and 1989. There was a decrease from a high of 8.2 Mt in 1978 and 1979 as shown in Table 1 to about 4.5 Mt for the period 1986 to 1989 as shown in Table 3. The cost of lime increased from about $30/t in 1975 to about $57/t in 1985, but remained fairly constant at about $60/t in constant 1985 dollars. In 1989, the value of metallurgical lime was about 50 to $55/t.

Other Flux Materials

Other major flux materials used in ironmaking and steelmaking include fluorspar, alumina, and siliceous sources. Fluorspar is largely imported to the United States from Mexico, China, and the Republic of South Africa. The USBM publishes trends in fluorspar production and consumption as shown in Table 1 (Anon., 1987).

Table 2. Quantity (kt) and Value ($1 000) of Crushed Limestone and Dolomite Sold or Used Within the Chemical and Metallurgical Industries in the United States in 1989, by Use

	Limestone		Dolomite	
Use	Quantity	Value	Quantity	Value
Lime manufacture	14 330	83 600	308	1 400
Flux stone	4 262	19 600	635	2 600
Total, all uses	731 586	3 234 300	44 715	217 000

Adapted from USBM, Tepordei (1991).

About 25% of total fluorspar demand was for crude steel production. Between 1975 to 1983, fluorspar demand for crude steel production decreased from about 470 ktpy to 120 ktpy as shown in Table 1. The price doubled from about 86 to $181/t during the same period; the price rose from 162 to $195/t in constant 1985 dollars.

In ironmaking, small amounts of alumina-bearing and siliceous materials are used. In the United States there is a shortage of high-grade, domestic alumina sources except for aluminiferous clays which contain silica. Thus, bauxite must be imported from Greece, Turkey, or Jamaica. In contrast, siliceous materials are plentiful. Silica sources for the blast furnaces include crude ore (taconite) from the iron mines and local gravel. Local sands and other fine siliceous materials can be used to increase the silica content of sinter. In the nonferrous industries, fluxes are largely siliceous, and often lean ores or nearby rock can be used as flux if the impurities are low. In some instances, high grade silica rock is used. Gypsum has been used as a source of lime and sulfur in nickel smelting (Habashi, 1986).

RAW MATERIALS

The selection of flux for a particular process requires specification of the chemistry of the flux materials required to form a slag of the required composition to attain a desired effect. Ideally, only pure substances would be selected, however, these are seldom available in nature. In general, the level of impurities in the flux should be as low as possible because the greater the amount of impurities, the less effective will be the flux, and the greater the amount that will be required. In addition, some minor impurities can

Table 3. Quantity (kt) and Value ($1 000) of Lime Sold or Used in the Metallurgical Industries in the United States, by Use

Use	1986 Quantity	1986 Value	1987 Quantity	1987 Value	1988 Quantity	1988 Value	1989 Quantity	1989 Value
Metallurgy	9	467	4.5	218	W	316	W	W
Steel, BOF	3 338	175 300	3 701	189 700	3 845	182 900	3 563	180 720
Steel, Electric	801	41 530	689	35 240	860	44 530	888	46 294
Steel, Open Hearth	111	5 940	131	6 733	45	2 190	58	2 877
Other[a]	822	50 490	2 511	125 000	2 127	116 000	3 211	178 958
Total steel	4 250	222 770	4 521	231 673	4 750	229 620	4 509	229 891
Total (Chemical & Industrial)	11 455	637 800	12 789	682 400	13 424	686 900	13 759	730 800
Total, all uses	13 151	761 200	14 294	789 700	15 492	821 700	15 582	855 900

Adapted from USBM, Ober (1989), Miller (1990).
W = withheld to avoid disclosing company proprietary data.
[a]Includes metallurgical applications including briquetting, chrome, ferroalloys, ladle desulfurizing, magnesium metal, manganese, pelletizing, chemical and industrial uses specified as W above, as well as many other non-metallurgical uses (see original tables for detail).

have significant detrimental effects on the process or process equipment. After the chemistry is specified, the size of flux will be determined largely by the handling and gas flow requirements of the particular process, and to a lesser extent, on the size of flux that is available. Geographic location and economics might dictate that a flux from a particular source and with a particular chemistry be selected. If the desired chemical or physical specifications important for a given process can not be attained from the most economical source, a new source might have to be found, or an alternate process might have to be developed.

Since 90% of all metal production is iron and steel, the major fluxes consumed will be those used in ironmaking and steelmaking, that is, limestone, dolomite, lime, fluorspar, and to a small extent, siliceous sources. Many of the same considerations that apply to the fluxes used in ferrous smelting apply to fluxes for nonferrous smelting. Although limestone and dolomite are used largely in ironmaking and steelmaking, some small amounts are used in nonferrous smelting, particularly in smelting and refining of copper and lead ores where the ores are generally acidic. Foundry cupolas also use some stone (Boynton, 1980).

Chemistry of Limestone and Dolomite

Limestone and dolomite are used in smelting iron ores specifically to supply lime (CaO) and magnesia (MgO) to form a slag with the acid components, particularly silica (SiO_2) and alumina (Al_2O_3). Typical chemical analyses for limestone, dolomite, and their respective calcined products are shown in Table 4. The ideal flux will be low in acids (silica, alumina and sometimes titania and iron oxide) as well as low in sulfur (S), phosphorus (P), alkali metals (sodium and potassium), and halides (chlorides and fluorides). All phosphorus in ironmaking raw materials including iron ores or agglomerates, coke, and fluxstone is reduced to metal in the blast furnace and appears in the iron product, therefore, phosphorus must be minimized in the flux. This is particularly true with recycled slags, and it is the phosphorus content that determines the amount of steelmaking slag that can be recycled to ironmaking. A major purpose of the ironmaking slag is to remove sulfur, therefore sulfur in flux as well as other materials should be low. Alkali metals are generally detrimental to blast furnace operation often forming deposits on the furnace walls, therefore alkali inputs from raw materials should be minimized. During the production of fluxed pellets or sinter, the alkali metals in combination with sulfur, chlorides, and fluorides have been found to be extremely detrimental to process equipment in some pellet and sinter plants.

Table 4. Typical Analyses of Limestone, Dolomite, and Lime Fluxes

Component	Limestone Blast Furnace[a]	Limestone Sinter Plant	Dolomite Blast Furnace[a]	Dolomite Sinter Plant	Burnt Lime High-Calcium	Burnt Lime Dolomitic
	(one year average, % by weight)				(calculated)	
$CaCO_3$	95.3	93.8	54.5	52.4		
$MgCO_3$	3.1	3.6	42.0	40.0		
CaO	53.4	52.5	30.6	29.4	88.5	56.0
MgO	1.5	1.7	20.1	19.1	2.5	36.8
R_2O_3[b]	0.3	0.4	0.3	0.4	0.5	0.5
SiO_2	0.7	1.8	2.6	6.8	1.2	4.7
	(typical, % by weight)					
Fe_2O_3	0.20	0.30	0.2	0.3		
Al_2O_3	0.30	0.20	0.3	0.3		
Mn	0.01	0.02	0.01	0.03		
P	0.01	0.01	0.01	0.01		
S	0.03	0.04	0.05	0.03		
K_2O	0.10	0.10	0.10	0.10		
Na_2O	0.02	0.02	0.02	0.02		
LOI[c]	43.40	46.10	6.00	1.00	1.0	2.0

[a]Also typical of flux used in fluxed pellets and as stone for lime production.
[b]$R_2O_3 = Fe_2O_3 + Al_2O_3 + Cr_2O_3 + TiO_2$
[c]Loss-on-Ignition

Silica addition to the blast furnace is often required to obtain the proper ratio of basic to acid components in the slag, and addition of a siliceous source enables accurate control of this ratio. Historically, in traditional blast furnace practice, up to 5% silica in the flux was tolerated and 1 to 3% was common (Gault and Ames, 1960). Today, the levels are lower and the amount tolerated depends on whether the flux is used for sinter or for direct charging, and what the levels of silica are in other burden materials. The allowable level depends on the desired slag chemistry and slag quantity required for control of the furnace and the sulfur and alkali.

The silica content in flux used for fluxed pellets should be as low as possible because the total silica content of the pellets is carefully monitored. A silica content of less than 1% in the flux is commonly desired. Furthermore, uniformity of composition over time is important. The silica content of the flux adds to the silica content in the fluxed agglomerates, and therefore more flux is required, and more energy is required to calcine the additional flux.

High silica is less of a problem in flux used for sintering, as the sinter can be used as a vehicle for introducing small amounts of silica to the blast furnace in a controllable way, and energy is available from combustion of coke fines and from oxidation of mill scale (ferrous oxide) in the sintering process.

The magnesia content of limestone added to the blast furnace is often not critical because both magnesia and lime are added to form a slag. The amount that can be tolerated depends on the magnesia contents of all burden materials and the target slag chemistry. Generally, a higher magnesia content keeps slag fluid over a wider temperature range (Gault and Ames, 1960, Rosenqvist, 1974). Dolomite might be added to provide sufficient magnesia to produce slag of a certain specification, for example, for use as aggregate. Magnesia added in sufficient amount increases the melting point, and this effect is used to advantage when making fluxed pellets for the blast furnace. The magnesia content of the limestone must be known with certainty when producing blends of limestone and dolomite for use in fluxed agglomerates.

Physical Properties of Limestone and Dolomite

Traditional ironmaking practice has relied on direct charging of the iron blast furnace with flux materials of up to 15 cm in size. However, more recent practice that recognizes the need for a uniformly sized and permeable burden requires a size more compatible with other burden materials, and stone as fine as 5 by 1.25 cm has been used. The location in the blast furnace where complete calcination occurs can be regulated by changing the size of stone (Lankford, Jr., et al., 1985). Typically, flux added to sinter is in the range of −6.35 to −3.17 mm in size with 90% coarser than 150 mesh (0.104 mm). Some iron producers have adopted the use of fluxed pellets, which requires that the stone be ground to 60 to 80% passing 200 mesh (0.074 mm), a size more compatible with the formation of pellets from fine concentrates. The size ranges of limestone and dolomite required for the blast furnace, lime plant, sinter plant, and fluxed pellet plant are shown in Table 5.

Thermal decrepitation and physical degradation are not desirable because the permeability of the furnace burden is reduced by the presence of fines. Experience has shown that fine-grained stone decrepitates less than coarse-grained stone in the blast furnace (Gault and Ames, 1960). Resistance of the stone to physical degradation during handling and transportation is also important to minimize the amount of fines formed. When the fines will be deleterious to the process, they must be removed by screening. If the fines do not have an alternate use, the cost of the flux is effectively increased. A drop test from heights approximating those in handling of the stone can be used to estimate the expected amount of degradation during handling and transportation (Fagerberg and Sanberg, 1973).

Many standard tests for characterizing lime and limestone (as well as dolomitic lime and dolomite) have been developed by the American Society for Testing Materials (ASTM) (Anon., 1988). A list of standard ASTM tests commonly applied to limestone and dolomite are listed in Table 6. Accurate sampling of the stone is often a problem due to the large size or wide range of sizes. Sampling of stone is described in ASTM tests C-50 and D-75. Chemical analysis of limestone and dolomite are easily accomplished according to standard procedures defined in ASTM C-25 and by published or proprietary methods using modern analytical techniques. Physical testing is defined in ASTM C-110. The physical test most often done is sizing or screening of the stone to determine the size distribution as described in ASTM E-11, C-136, E-276, and E-389. Additional tests that might be applied to determine the degradation characteristics are the Los Angeles test (ASTM C-131, C-535) and the ASTM tumble test (ASTM E-279).

Table 5. Size Analyses of Typical Flux Stone for Blast Furnace Sinter Plant, Lime Plant, and Fluxed Pellet Plant

	(% passing)					
	Blast Furnace or Lime plant stone		Mixed Blend	Sinter Flux		Pellet Flux
Size	Limestone	Dolomite	50:50[a]	Limestone	Dolomite	50:50[b]
cm						
7.620			99.6			
6.350	87.6		99.0			
5.080	46.2	88.7	91.0			
4.445	18.7	72.7				
3.810	9.1	50.5	64.6			
3.175	4.4	26.4				
2.540	2.6	14.8	15.7			
1.905	1.7	2.0				
1.270			2.5			
0.952				99.8	100.0	
0.635			1.2			
mm						
4.699				97.5	97.8	
3.327				90.6	86.1	
1.651				66.0	58.6	
0.589				20.3	20.0	
0.295				8.2	10.0	99.9
0.208						99.3
0.147				2.4	4.7	90.4
0.074				0.9	2.4	65.9
0.053						58.2
0.043						52.2
0.038						47.2
0.026						42.0

[a]Feed to crusher at fluxed pellet plant (50% limestone, 50% dolomite), [b]Ball Mill Grinding.

Chemical Properties of Lime

Limestone and dolomite are calcined or heated to drive off the carbon dioxide prior to use in steelmaking. Calcination is usually done in rotary kilns or rotary kiln-shaft combinations. Typically, the temperatures are 900 to 1 100°C. Calcination is strongly endothermic and requires energy input. The reaction proceeds according to:

$$CaCO_3(s) = CaO(s) + CO_2(g) \text{ for limestone, and}$$

$$(Mg,Ca)CO_3(s) = (Mg,Ca)O(s) + CO_2(g) \text{ for dolomite}$$
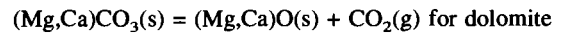
where (s) is a solid, and (g) is a gas. In the blast furnace, calcination of limestone begins at temperatures over 800°C and dolomite decomposition typically begins at 700°C or lower (Ricketts, 1992). Thermal requirements are discussed in the literature (Boynton, 1980).

High-calcium lime, and to a lesser extent dolomitic lime, are typically used as fluxes in steelmaking and in some nonferrous smelting and refining processes. The chemistry of lime is specified more closely in steelmaking than in ironmaking. Typical analyses of lime and dolomitic lime are shown in Table 4. In steelmaking, high calcium lime with a low silica content is specified because the lime is used to combine with the silica formed by oxidation of silicon in the steel bath. Dolomitic lime is added in steelmaking to control the MgO content to minimize wear of the basic refractory lining.

The available base for reaction with acidic components is im-

Table 6. ASTM Standard Physical and Chemical Tests and Definitions Applicable to Limestone, Dolomite, and Fluorspar

ASTM No.	Description
C 25	Standard Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime.
C 29	Unit Weight and Voids in Aggregate.
C 50	Sampling, Inspection, Packing and Marking of Lime and Limestone Products.
C 51	Standard Definition of Terms Relating to Lime and Limestone.
C 70	Surface Moisture in Fine Aggregate.
C 110	Physical Testing of Quicklime, Hydrated Lime, and Limestone.
C 125	Definition of Terms Relating to Concrete and Concrete Aggregates.
C 127	Specific Gravity and Absorption of Coarse Aggregate.
C 128	Specific Gravity and Absorption of Fine Aggregate.
C 131	Standard Test Method for Resistance to Degradation of Small-Size Coarse Aggregate by Abrasion and Impact in the Los Angeles Machine.
C 136	Sieve or Screen Analysis of Fine and Coarse Aggregates.
C 184	Fineness of Hydraulic Cement by the 150 μm (No. 100) and 75 μm (No. 200) Sieves.
C 204	Fineness of Portland Cement by Air Permeability Apparatus.
C 294	Descriptive Nomenclature of Constituents of Natural Mineral Aggregates.
C 295	Petrographic Examination of Aggregates for Concrete.
C 430	Fineness of Hydraulic Cement by the 45 μm (No. 325) Sieve.
C 535	Standard Test Method for Resistance to Degradation of Large-Size Coarse Aggregate by Abrasion and Impact in the Los Angeles Machine.
C 566	Total Moisture Content of Aggregate by Drying.
C 702	Reducing Field Samples of Aggregates to Testing Size.
C 786	Fineness of Hydraulic Cement and Raw Materials by the 300 μm (No. 50), 150 μm (No. 100), and 75 μm (No. 200) Sieves by Wet Methods.
D 75	Sampling Aggregates.
E 11	Wire-Cloth Sieves for Testing Purposes.
E 12	Standard Definitions of Terms Related to Density and Specific Gravity of Solids, Liquids, and Gases.
E 276	Particle Size or Screen Analysis at No. 4 (4.75 mm) Sieve and Finer for Metal Bearing Ores and Related Materials (including wet methods).
E 279	Tumbler Test for Iron Ore Pellets and Sinter.
E 382	Determination of Crushing Strength of Iron Ore Pellets.
E 389	Particle Size or Screen Analysis at No. 4 (4.75 mm) Sieve and Coarser for Metal Bearing Ores and Related Materials.
E 463	Silica in Fluorspar by the Silico-Molybdate (Photometric) Method.
E 815	Test Methods For Calcium Fluoride in Fluorspar by Complexometric Titration.

From ASTM (Anon., 1988).

portant (Lankford, Jr., et al., 1985, Peters, 1982). The available base (AB) is calculated as:

$$CaO/(SiO_2 + R_2O_3) \text{ or } CaO + MgO\text{-}SiO_2\text{-}R_2O_3\text{-}LOI$$

where R_2O_3 is the sum of the Fe_2O_3, Al_2O_3, and TiO_2.

The sulfur content of the lime should be low, and absorption of sulfur originating with both the stone and fuel during calcining can be a major problem. The sulfur level in the calcined lime is controlled by regulating the oxygen content in the calcining system

exit gas. Gypsum in the flux stone is not desirable because it is difficult to decompose, but sulfur in pyrite or pyrrhotite is generally removable. Sulfur also occurs as organic sulfur in graphite within the stone. Sulfur levels of 0.03 to 0.06% in the lime are typical.

After calcining, lime is hygroscopic which means it readily absorbs water from the air and slakes to form calcium hydroxide. In addition, some uptake of carbon dioxide and sulfur dioxide can occur thereby forming a dense layer of calcium carbonate and/or gypsum on the surface. This layer can adversely affect the subsequent reaction rate of the lime. In addition, if the lime is not completely calcined, a core of unreacted limestone (or dolomite) will remain in the center of the larger lime (or dolomitic lime) pieces. The unreacted core and the adsorbed water and carbon dioxide will result in a "loss-on-ignition" or LOI when the lime is heated. The lime for steelmaking generally requires a low LOI of 2 to 4% or less, and some plants require an LOI not exceeding 0.5% (Boynton, 1980).

Physical Properties of Lime

The size of lime used in steelmaking is typically 37 by 6.35 mm The particle size of the lime and dololime fluxes added to steelmaking vessels is important because if particles are too fine, they will be removed by the intense gas flow above the steelmaking vessel before they can react to form slag. Typically, all particles 3 mm and less in size will be removed. Therefore, considerable effort is made to achieve a low fines content in the lime used. However, lime degrades by physical handling and by degradation due to hydration and carbonation in storage. Lime placed in storage might contain as little as 5% to as much as 20% of material finer than 3.17 mm, yet after several days of storage, and depending on the relative humidity and natural characteristics of the lime, fully one third of the lime can degrade, and up to one half will exist as fines after handling and transfers before the steelmaking vessel. Some stones characteristically produce significant dust during calcining resulting in plugging of baghouse filters.

Several steelmaking processes use bottom blowing and some use combined top and bottom blowing so that much finer flux can be used as an injectant. Fine lime can be pneumatically conveyed by oxygen or a carrier gas and injected through tuyeres (openings) in the vessel bottom. The high surface area of the fine lime promotes rapid slag-metal reactions. The sizes of lime typically used in the injection process are about the same as those shown for Pellet Flux in Table 5, or finer (Koros, 1991).

The reactivity of the lime added to the steelmaking vessel is important. One test often used to estimate the reactivity of the lime in steelmaking is the ASTM water reactivity test (ASTM C-110) (Schlitt and Healy, 1970). In this test, the lime is broken to −6 mesh (3.33 mm), a prescribed amount is stirred into water held in an insulated bottle to retain the exothermic heat of reaction in the system, and the temperature rise of the water with time is recorded. The time of reaction and the temperature rise are used to indicate the reactivity of the lime. The American Water Works Association Standard B2-2 is similar. Although some correlation of water reactivity with slag formation has been reported, a crucible test is probably more directly related to lime behavior in steelmaking (Limes and Russel, 1970).

Requirements for Fluorspar

Fluorspar or calcium fluoride (CaF_2) is used as a flux along with lime to improve the fluidity of slag in steelmaking and subsequent ladle metallurgy processing. Typical consumption of fluorspar in steelmaking is 2 to 10 kg/t or 5 to 10% of the lime added (Peters, 1982). Fluorspar is also used with lime in electroslag

Table 7. Composition of Metallurgical Fluorspar (Dry Basis)

Component	(% by weight)		
	High-Grade	Medium-Grade[a]	Low-Grade[b]
CaF₂	92.7	89.1	82.0
SiO₂	3.5	3.9	8.9
Fe	0.09[c]		
S	0.05[c]		
CaCO₃	3.5	4.6	4.2
Effective CaF₂	83.9	79.3	59.7

[a]Gravel Size; minus 6.35 cm, plus 0.95 cm.
[b]Screen Fines; 78% minus 6.35 mm and plus 100 mesh (0.147 mm); 11% -325 mesh (.043 mm)
[c]Oxides of iron and aluminum and sulfur can sometimes reach 1% in lower grade products.

refining in a ratio of about 70 parts fluorspar to 30 parts lime (Duckworth and Hoyle, 1969). The purpose in electroslag refining is to form a very conductive slag with the required melting point.

The specification for metallurgical-grade fluorspar is 72% minimum effective fluorspar where the effective fluorspar is calculated from:

$$\text{Effective } CaF_2 = CaF_2 - (2.5 \times SiO_2)$$

The main impurity in fluorspar is silica, the balance of impurities generally being calcium carbonate, barite, lead, and zinc. Analysis is done by ASTM E815 and E463 (Anon., 1988) or by other generally accepted analytical methods. The chemical analyses of typical fluorspars are shown in Table 7.

The fluorspar can be added as lumps, gravel-sized material, or as fines incorporated in briquettes. Sizes of gravel and screen fines are shown in the footnotes to Table 7. Typically, 5 to 15% fluorspar fines would be added to briquettes made with recycled slag fines or other steelmaking ingredients. The latter form is often preferred to achieve better mixing of fluxes and better reaction with the slag. As with lime, any loose fines present will be lost during the blow.

Other Materials

Silica-bearing materials are sometimes added to the blast furnace to control the process basicity and counteract over addition of basic fluxes. Additions are generally kept to a minimum. The chemistry of the source should be compatible with the process, and deleterious elements such as alkali metals, phosphorus, and sulfur should be avoided. In ironmaking, typical silica sources are low grade taconite ore, flint clay containing alumina, sandstone, gravel, or used brick. Specifying the material as low grade with respect to silica allows a larger, measurable, and more controllable quantity to be added. For example, addition of taconite ore containing 50% silica and 35% iron allows additional iron units to be added to the furnace while adding a larger volume of material than if adding pure silica. In copper smelting, low grade ores or rock are used, but sometimes high grade silica is used. In any process, the criteria for size is that the material should be of a size compatible with the process and fine enough to react rapidly, but not so fine that it will cause permeability problems or be lost as dust.

TECHNOLOGY

The successful application of a slag in a metallurgical process depends on the slag chemistry and properties of the molten slag

which are obtained by selecting the proper fluxes. The properties of a slag that are important are melting point, viscosity, surface tension, density and chemical activities of the components present. In electric smelting practices, conductivity is also important. These parameters all depend on a knowledge of the composition. The effects of composition on melting temperature and other properties are often described through temperature-composition diagrams (phase diagrams) and property-composition diagrams. In practice, it has been found convenient to use index values to describe composition requirements for a given process. Thorough discussions of the properties of metallurgical slags can be found in the literature (Derge and Tenenbaum, 1951, Turkdogan, 1983, Rosenqvist, 1974, Lankford, Jr., et al., 1985, Elliott, 1984).

Properties of Slags

Melting Point: The most common fluxes used in smelting and refining are lime (or limestone) and silica. The melting point of pure lime is higher than the process temperatures during smelting of iron ores or refining of steel. However, it has been found that when lime is added to other components such as silica, the melting point is lowered and a liquid phase forms. This phenomenon can be extended to multi-component systems. In most systems, there are more than two components, and interactions between components become complex. It has been found convenient to represent the interactions on ternary or 3-component composition diagrams. Phase diagrams for many systems including those in ironmaking, steelmaking, and nonferrous smelting and refining can be found in a series of publications entitled *Phase Diagrams for Ceramists* (Levin et al., 1956, 1969).

Iron blast furnace slags are generally represented in the CaO-SiO₂-Al₂O₃ ternary system. Typical iron blast furnace slag contains 32 to 42% silica (SiO₂), 7 to 16% alumina (Al₂O₃), 32 to 45% calcia (CaO), and 5 to 15% magnesia (MgO) (Lankford, Jr., et al., 1985). The composition of iron blast furnace slag is generally controlled to maintain a composition with about 10% alumina (some practices contain greater amounts) to achieve a relatively constant melting point and liquid slag over a wide range of lime and silica variations. The melting point is typically 1 400 to 1 500°C. Ferrous iron will react with silica at much lower temperatures than calcia and alumina, and local melting can occur in the lower part of the shaft of the iron blast furnace. One purpose of flux in fluxed pellets is to avoid early melting that results from the formation of iron silicate (Fe₂SiO₄ or fayalite) by preferentially reacting silica in the pellets with lime and magnesia (Taguchi et al., 1980, Ranade, 1992). In non-ferrous smelting, iron silicate slags that melt near 1 200°C are formed.

Viscosity: A major component of many slags is silica which can form complex silicate networks in the molten state. These networks comprise chains of silica molecules, and this results in very viscous flow conditions. Silica also melts at a high temperature, therefore, separation and movement of silica is difficult. It has been found that the addition of lime breaks up the silicate networks, lowers the melting point, and enhances the movement of the slag. Therefore, the viscosity of iron blast furnace slags decreases with increasing lime addition and increases with increasing silica and alumina (Rosenqvist, 1974). Addition of a basic oxide such as magnesia (MgO) has only a small effect on viscosity and is used to minimize variability over a range of compositions. If sufficient lime is present to form dicalcium silicate, viscosity will increase sharply. In basic slags, a small decrease in temperature will increase viscosity a small amount, however, as solid phases such as dicalcium silicate precipitate, viscosity will increase rapidly (Rosenqvist, 1974).

In steelmaking slags, calcined lime is added as a flux to react

with silica and phosphorus oxidized from the steel bath. The reaction of the lime is sometimes impeded due to formation of a dicalcium silicate or calcium ferrite shell on the lime particles. Fluorspar (CaF_2) is often added to the steelmaking vessel to aid in dissolution of the lime and to reduce the viscosity of the slag. The mechanism is not precisely known, however, it is thought that the fluorspar attacks the coating on the lime (Peters, 1982). Fluorspar melts at 1 386°C and dicalcium silicate melts at over 2 000°C, but when approximately equal portions of fluorspar and di-calcium silicate are mixed, the melting point decreases to below 1 200°C. (Levin et al., 1956, 1969).

Surface Tension: Surface tension of slag is important, but is not often used to characterize slags, probably due to the difficulty of measurement. However, surface tension affects the wetting of both metals and refractories by slags and this affects the rates at which various components dissolve in the slag and the ease of separation of slag and metal. Foaming during blowing in basic oxygen steelmaking and also in the electric furnace is affected by surface tension. The surface tension decreases with increasing silica content, with addition of alkali oxides, calcium sulfide, and phosphoric oxide, and with an increase in temperature. Lime, iron oxide, and alumina increase the surface tension of slag (Rosenqvist, 1974).

Density: Density can be controlled to achieve separation of metal and slag by adjusting the proportions of components of differing densities. In ironmaking, the slag density increases with increasing lime and iron contents, but is not specifically controlled. In copper smelting, where the product is a matte of lower density than metal, the separation of slag and matte is enhanced by decreasing the density of the iron-rich slag by addition of lime (Rosenqvist, 1974).

Activity: The activity of a species in a slag is a parameter that is a function of both concentration and temperature and determines how a particular species will react with other components in a given system. Values of thermodynamic activity can be used to predict the equilibrium in the process. Activity (a_i) is related to the more familiar concentration term expressed as the mole fraction (X_i) through the activity coefficient (γ_i):

$$a_i = \gamma_i \cdot X_i$$

For ideal gases, the activity is the partial pressure (p_i). A thorough discussion of thermodynamics of slags can be found in the literature (Derge and Tenenbaum, 1951, Coudurier et al., 1985, Lankford, Jr., et al., 1985, Turkdogan, 1983, Elliott, 1984). In general, activity can't be predicted, and the activity or the activity coefficient is usually measured experimentally. Values for particular systems can be found in the literature.

Index Values

The majority of slags can be described as either basic slags as used in ironmaking and steelmaking or acid slags as used in nonferrous smelting. The desired composition of a slag in a metallurgical system is often defined by index values that express the acidity, basicity, or the capacity of a slag to perform a desired function. In practice, the composition of the slag is controlled by adjusting the proportions of flux added to combine with impurities or gangue to yield a desired index value. Common index values are basicity or total basicity (TB), V-ratio, optical basicity (OB), and sulfide capacity (C_s).

Basicity: The general description of basicity is the ratio of basic oxide components to acid oxide components in the slag. Care must be exercized in specifying which basicity definition is being used. Because lime and silica are the most prevalent species in basic

slags, the definition of basicity (B) is often given as the lime-to-silica ratio:

$$B = CaO/SiO_2$$

where the weight percent of the chemical species is used to compute the ratio. This ratio is also called the C/S ratio in the manufacture of fluxed pellets. The magnesia-to-silica ratio or M/S ratio is sometimes also specified for fluxed pellets.

The most often used definition of basicity in blast furnace practice is the four-component basicity or total basicity (TB) defined as:

$$TB = (CaO + MgO)/(SiO_2 + Al_2O_3)$$

The total basicity is sometimes modified to include titania (TiO_2) as an acid.

V-Ratio: In steelmaking, the basicity is often referred to as the V-ratio which expresses the ability of a slag to desulfurize or dephosphorize the steel bath. The V-ratio is usually defined as one of the following:

$$CaO/SiO_2; \quad (CaO + MgO)/SiO_2; \quad or \quad (CaO - 4P_2O_5)/SiO_2$$

Sometimes, the V-ratio is defined the same as total basicity given above.

Optical Basicity: The optical basicity is sometimes used to characterize a slag for correlation with desulfurization (Sosinsky and Sommerville, 1986, Blattner, 1992). The optical basicity (OB) is defined as:

$$OB = \frac{(\%CaO + 1.11\%MgO + 0.915\%SiO_2 + 1.03\%Al_2O_3)}{(\%CaO + 1.42\%MgO + 1.910\%SiO_2 + 1.69\%Al_2O_3)}$$

Sulfide Capacity: Slags are desulfurized primarily by reaction with lime to form calcium sulfide which dissolves in the slag. The ability of the slag to dissolve sulfides is expressed as the sulfide capacity (C_s) which is:

$$C_s = (\%S)(P_{O_2}/P_{S_2})^{0.5}$$

where P_i is the partial pressure of component i. Sulfide capacity can be expressed in terms of optical basicity (OB) and temperature as follows:

$$\log C_s = [(22690 - 54640OB)/T] + 43.6OB - 25.2$$

where T is the temperature in degrees Kelvin (°K) over the range 1 400 to 1 700°C. The sulfide capacity of a slag increases with increasing lime (CaO), and a low silica activity (a $_{SiO_2}$) is desirable.

USES

Fluxes are used at various stages in the production of iron and steel. Iron used for steel production is produced in the iron blast furnace largely by traditional practices described in the literature (Lankford, Jr., et al., 1985). As a result of fairly recent studies of iron-bearing raw materials and dissections of the burdens of iron blast furnaces, the high temperature properties of the iron-bearing burden materials have been improved (Taguchi et al., 1980, Yamoaka et al., 1980). This has resulted in modifications to fluxing practice at some furnaces wherein flux is introduced to the furnaces through fluxed sinter and fluxed pellets rather than by direct charg-

ing. There has also been an increase in the use of external desulfurization of hot metal prior to steelmaking which allows greater flexibility in selection of furnace burden materials with respect to sulfur content, and greater flexibility in furnace operating practices for control of other furnace parameters (Stubbles, 1984). Steelmaking is largely accomplished in basic oxygen furnaces with the virtual phasing out of the open hearth process, although electric furnace steelmaking continues to increase. Modern steelmaking includes the treatment of steel in ladles for improved cleanliness, greater throughput in the steelmaking vessels, and shape control of inclusions in the continuous casting process which now dominates over ingot processing (Szekely et al., 1989). A variety of powder mixtures and prefused slags are used as mold fluxes in the continuous casting of steel (Branion, 1987). Fluxes are also used in smelting and refining of nonferrous metals.

Iron Blast Furnace

The modern iron blast furnace uses iron-bearing agglomerates, coke, and flux to produce hot metal. The flux, which is largely limestone and dolomite, provides basic elements (calcium oxide and magnesium oxide) to the furnace charge to form a slag with acid flux elements (silicon oxide and aluminum oxide) present in the iron-bearing agglomerates and coke. This slag provides a vehicle to remove the silica and alumina gangue that was introduced with the ore and coke, and sulfur that was introduced with the coke. Hot metal produced from the blast furnaces is further treated in transport vessels and in subsequent steelmaking operations to reduce impurity levels. These operations also require slags.

The limestone and dolomite flux used in the blast furnace can be added as lumps 2.5 to 7.5 cm in size, or can be added to iron-bearing agglomerates and charged to the furnaces as fluxed pellets or fluxed sinter. Agglomerates are large particles formed from smaller particles and fused at high temperatures to form a material that is readily handled and transported without formation of fines. The agglomerates are also designed to react in a predictable manner inside the blast furnaces. In the agglomerates, limestone and dolomite are ratioed to the silica and alumina. The ratio can be expressed as the basicity ratio discussed earlier, or as in fluxed pellets, the basicity might be calculated as the lime-to-silica ratio (C/S ratio) to reflect only the major components. A comprehensive overview of the use of raw materials in the blast furnace was recently published (Ranade, 1992).

The total basicity of iron blast furnace slags is typically between 1.05 and 1.15 to achieve a fluid slag with adequate capacity to remove sulfides, although ratios as low as 0.9 and as high as 1.4 are reported (Anon., 1989). Typically, fluxed pellet basicities will be between 0.7 and 1.7, and sinter basicities will be between 1.7 and 4.0. When the basicity of the agglomerates is higher than the basicity of the furnace, siliceous materials must be added to reach the required furnace slag basicity. Coke ash furnishes silica to the furnace, but additional siliceous material might be required. The basicity of the agglomerates is selected to obtain specific reducing and melting properties to improve furnace operation. The higher basicities for sinter are used when the primary function of the sinter is to provide calcined flux to the furnaces. At very high basicities, melting of the sinter can be a problem due to formation of dicalcium silicate.

The amount of flux charged directly to blast furnaces varies widely depending upon the amounts charged in fluxed agglomerates. The majority of blast furnaces operating in the United States with fluxed pellets and/or sinter charge 10 to 50 kg/t of hot metal. Those not using any fluxed burden materials are charging 100 to 250 kg/t (Anon., 1989). A typical blast furnace charge could contain 900 kg of pellets, 650 kg of fluxed sinter, 25 to 100 kg of recycled steelmaking slag, and 50 kg of dolomite depending upon the chemistries of the individual materials (Lankford, Jr., et al., 1985).

Typical blast furnace slag contains 32 to 42% silica (SiO_2), 7 to 16% alumina (Al_2O_3), 32 to 45% lime (CaO), and 5 to 15% magnesia (MgO) (Lankford, Jr., et al., 1985). The slag composition varies significantly between countries depending upon the chemistries of the raw materials available (Blattner, 1992).

With emphasis on consistent quality, high productivity, and lower cost hot metal from blast furnaces, improvements have been made in the type of burden and the characteristics of the agglomerates used. Furthermore, to minimize the heat lost in slag removed from the furnaces which requires expensive coke to be burned, a trend to lower slag volumes (actually, slag mass per unit of hot metal produced) has occurred. The lower slag volumes result from using agglomerates with low gangue contents and coke with low ash content. With lower gangue contents, lower limestone and dolomite consumption has resulted. Typically, 225 to 275 kg/t is normal practice, but many modern furnaces are approaching 200 kg/t. Some furnaces have reached 150 kg/t under special circumstances, while some are much higher (Anon., 1989, Blattner, 1992). With increased use of external desulfurization (described here), the lower limit is a function of furnace operating practice. Because slag is removed with the hot metal during tapping, slag removal is not independently controlled, and factors such as furnace size and design can affect the lowest possible slag volumes attainable. Also, there can be some economic tradeoffs, for example, less expensive high sulfur coals might be available for making coke, and this might offset the cost of using more flux.

The presence of alkali (sodium oxide and particularly potassium oxide) in the blast furnace can lead to operating problems such as degradation of coke and formation of scaffolds on furnace walls. These scaffolds can greatly reduce furnace permeability and can cause damage if they break loose. Alkali metal content in the furnace is regulated through selection of raw materials and through control of the basicity of the slag (Sciulli, 1992). Alkali removal is greatest with slags of low basicity. Typically, 60 to 80% of the alkali input will be removed with the slag.

External Treatment of Hot Metal

In the United States, external treatment of hot metal or pretreatment prior to steelmaking is most often done for desulfurization. This treatment, done in transfer cars or ladles, allows control of sulfur input to steelmaking, reduces the slag requirement in the steelmaking vessel, allows the use of higher sulfur raw materials in the blast furnace, and permits production of low-silicon hot metal. Thus, blast furnace performance can be improved (Stubbles, 1984, Szekely et al., 1989). Some common reagents used are magnesium, lime, and fluorspar. Limestone, calcium carbide, coke, sodium carbonate, salt-coated magnesium, and aluminum are sometimes used. The consumption of these reagents is on the order of 4 to 7 kg/t except for the salt-coated magnesium which is added at 0.5 kg/t (Szekely et al., 1989, Cameron, 1992). The thermodynamics of the process and practice at several plants are described in the literature (Pehlke, 1984, D'Orazio, 1984, Dukelow, 1984).

Simultaneous desulfurization and dephosphorization can also be accomplished with soda ash (sodium carbonate) or lime if the metal is low in silicon (Szekely et al., 1989). The sodium carbonate (Na_2CO_3) reacts with sulfur, silica, and phosphorus to form sodium sulfide (Na_2S), sodium silicate ($Na_2O \cdot SiO_2$), and sodium phosphate ($3Na_2O \cdot P_2O_5$) in the slag. An advantage of this process is that the sodium carbonate can be recovered and recycled, however, high refractory wear is typical (Yamamoto et al., 1980).

Oxygen Steelmaking

Steel is produced by refining hot metal for removal of carbon, silicon, and other impurities. Most steel is now produced by the

basic oxygen process (BOP) in which hot metal is contacted with oxygen in a basic oxygen furnace (BOF) to oxidize impurities (Lankford, Jr., et al., 1985). The oxidized impurities rise to the top of the hot metal and are absorbed in a slag. The slag is formed from lime and dolomitic lime with addition of other compounds such as fluorspar to improve fluidity. Fluorspar (calcium fluoride) is added in an amount of 2 to 10 kg/ton (Peters, 1982), either as lump or gravel-sized material, or as briquettes made with about 15% fluorspar fines combined with slag residues from the BOF. The amount of flux added is usually proportioned to the expected silicon content in a ratio often referred to as the V ratio described earlier. Typically, the V ratio is 2.5 to 4.0 (Peters, 1982). The use of lime in steelmaking has been described in the literature (Boynton, 1980).

The amount of flux added depends on the silicon, sulfur, and phosphorus contents of the metal, and the purity of the flux (Lankford, Jr., et al., 1985). Typically, 40 to 100 kg of lime/t of hot metal and 10 to 30 kg of dolomitic lime/t of hot metal are added to the BOF (Lankford, Jr., et al., 1985, Peters, 1982). The amount of lime required in steelmaking has been steadily declining due to the trend towards decreasing silicon content of hot metal, and lower manganese contents. The increased use of scrap and the use of external desulfurization have also resulted in lower flux consumption in steelmaking. A typical steelmaking slag will contain about 10 to 20% silica (SiO_2), 40 to 50% lime (CaO), 10% magnesia (MgO), 15 to 20% iron (mixed oxides), 2 to 5% alumina (Al_2O_3), and 10% manganese oxide (MnO) and other oxides. The iron oxide content will depend upon the carbon level attained in the metal, generally increasing with lower carbon levels.

A second function of flux in steelmaking is to provide a slag that is neutral with respect to the lining of the steelmaking vessel. The lining in basic steelmaking is typically magnesia brick. To help prevent erosion and dissolution of the brick, a level of magnesia, typically 5 to 12%, is maintained in the steelmaking slag (Boynton, 1980, Lankford, Jr., et al., 1985, Peters, 1982). This is also useful for controlling the viscosity of the slag. The solubility of magnesia is greater in acid slags, that is, as the V ratio decreases. The effect of magnesia on phosphorus removal is often debated.

Ladle Metallurgy

Reagents can be added to liquid steel in the transfer ladles for additional refining to remove sulfur, reduce metallic oxides, and condition the slag prior to casting. Additions can also be made for alloying and for shape control of inclusions in the cast product. Reagents similar to those for hot metal desulfurization are used, and are added at the top of the ladle or are injected. Metallic elements can be added in the form of wire. Typical reagents are magnesium, lime, alumina, aluminum, fluorspar, calcium carbide, calcium-silicon alloy, and prefused di-calcium aluminate (calcium-aluminate). Magnesium is often added in combination with lime. Typical addition rates are 1 to 5 kg/t (Szekely et al., 1989). Calcium-aluminate increases the extent of deoxidation of steel and has a high capacity for sulfides (Turkdogan, 1985). An exothermic synthetic calcium-aluminate mixture comprising 58% dry burnt lime, 30% hematite, and 12% aluminum powder might be added at tap (Gilbert et al., 1988).

Electric Furnace Steelmaking

Electric furnaces are used to make steel and ferroalloys from scrap, other ferroalloys, and alloying elements. Oxidation is accomplished by injection of oxygen or by the addition of iron oxide either as mill scale or iron ore. Carbon is added as coke, used carbon electrodes, or coal, and lime is added as flux. In the electric furnace route to making steel, a two stage process with both oxidation and reduction is used. This is required to achieve necessary purification of the metal and high retention of alloying elements. In alloy steels, many components are readily oxidized and will report to the slag in an oxidizing environment, but can be recovered in a subsequent reducing environment. Therefore, double-slag, slag-and-a-half, and single slag practices followed by ladle metallurgy have evolved (Reebel, 1950, Sharp, 1967, Peters, 1982, Lankford, Jr., et al., 1985). In a single slag practice, after the melt down the oxidizing slag is held in the furnace and the steel is removed and treated further in a ladle. In a double-slag practice, the slag and metal are held in the furnace and the slag composition is adjusted. In either practice, alloy additions are made prior to the second stage. In slag-and-a-half practice, the first slag is removed and a lime-fluorspar slag is added to the electric furnace (Lankford, Jr., et al., 1985)

For oxidizing slags, limestone can be added, but calcined lime is most often used for slag formation. Limestone and coke are added in some practices to help create a foaming slag to protect refractories and to improve power efficiency. Lime and dolomitic lime are also added to protect the furnace refractories. Lime addition is 15 to 50 kg/t (Boynton, 1980). Other slag-forming ingredients are fluorspar, silica sand, crushed coke, and aluminum. During melting, oxidation of carbon occurs, and oxidation of phosphorus, silicon, manganese, and chromium results in removal to the slag. The V-ratio is controlled to over 2.5 in the melt down stage and a range of 2 to 4 is typical (Lankford, Jr., et al., 1985). The basicity depends on the silicon in the charge and in the flux added. The iron oxide in the slag is inversely related to the carbon in the bath as in oxygen steelmaking. An oxidizing melt down slag might contain 40 to 50% lime (CaO), 12 to 20% silica (SiO_2), 5 to 15% iron oxide (FeO), 3 to 10% alumina (Al_2O_3), 2 to 12% magnesia (MgO), and 5 to 15% manganese oxide (MnO) (Peters, 1982, Lankford, Jr., et al., 1985). Generally, 40 to 50% lime (CaO) is required for good sulfur removal (Lankford, Jr., et al., 1985).

The second stage can be done in a mildly reducing slag in a ladle in which a basic, non-oxidizing $CaO-Al_2O_3-SiO_2$ slag is built up from additions of lime, dicalcium aluminate and aluminum. During the second process stage, metal oxides in the slag are reduced and sulfur enters the slag as calcium sulfide, particularly in low iron oxide slags. In the double-slag electric furnace practice, a finishing or deoxidizing slag is formed by adding coke to react with lime to form a calcium carbide slag. High purity of both the coke and lime are desirable. Fluorspar equal to about 10% of the lime is added to increase reaction with lime and increase fluidity (Sharp, 1967). Silica is sometimes added, and alumina is sometimes added in place of fluorspar. The slag quantity is generally about 2 to 3% of the metal. A typical reducing slag might contain 55 to 70% lime (CaO), 15 to 25% silica (SiO_2), 1 to 3% alumina (Al_2O_3), 3 to 12% magnesia (MgO), and 0.5 to 2% FeO and MnO (Peters, 1982).

Continuous Casting

Fluxes are used during the continuous casting of steel and during bottom pouring of ingots. These fluxes are often referred to as *mold powders*. The fluxes are either mixtures of compounds or fused synthetic slags formulated to provide thermal insulation and prevent solidification in the mold, prevent oxidation, absorb oxide inclusions, provide lubrication at high temperature, and maintain uniform heat transfer. Important physical properties are flowability, melting rate, viscosity, crystallization temperature, inclusion absorption capacity, and insulation characteristics. The mold fluxes are largely silica based with additions of lime, alumina, fluorspar, alkali metal oxides and carbon. The fluxes are used both as raw mixtures (synthetic flux) and in premelted and sintered forms. The particle sizes range from −10 mesh (1.5 mm) granules to 90% −200

mesh (0.074 mm) powders. Typical mold fluxes contain 17 to 56% silica (SiO_2), 2 to 45% lime (CaO), 0 to 25% alumina (Al_2O_3), 0 to 15% fluorine (F_2), 0 to 10% iron oxide (Fe_2O_3), 0 to 20% borate (B_2O_3), 0 to 25% alkali metal oxides (Na_2O, K_2O, Li_2O), and 0 to 30% carbon (C). The amounts vary widely to attain the desired function. The basicity (CaO/SiO_2) is typically 0.65 to 1.67. Consumption of mold fluxes is 0.3 to 0.8 kg/t in continuous casting and 1 to 3 kg/t in ingot casting (Branion, 1987, McCauley, 1987).

Nonferrous Metals

The use of fluxes in nonferrous smelting is described in depth in the literature (Turkdogan, 1983, Rosenqvist, 1974, Habashi, 1986, Moore, 1981). Nonferrous slags differ from ironmaking and steelmaking slags because they are based largely on formation of iron silicate rather than calcium-aluminum silicate. A typical nonferrous slag will contain 30 to 55% iron oxide (FeO), 30 to 45% silica (SiO_2), and less than 10% lime (CaO), although there will be variation around these numbers depending upon the system. Phase diagrams of typical nonferrous systems showing the compositional ranges of slags can be found in the literature (Coudurier et al., 1985, Rosenqvist, 1974). In copper smelting, silica is the flux used in the largest amount, but lime is also added to modify slag viscosity and density. Limestone is also used in small amounts to aid in refining metallic copper, lead, zinc, tin, and antimony (Boynton, 1980). Limestone purity and particle size are generally similar to those used in ironmaking and steelmaking, but high-calcium limestone is most often used. Both high grade siliceous materials and lower grade siliceous ores are used as fluxes along with limestone. An overview of the technology applicable to smelting and refining of copper, lead, nickel, and other nonferrous metals was recently published (Peacey, 1989).

Copper: Copper occurs as both oxide and sulfide minerals, and smelting is used to recover copper from the sulfide ores. Many copper sulfide ores contain iron that must be fluxed, and typically, silica is used to flux the iron and form an iron silicate slag (fayalite). During smelting, the sulfur combines with copper and some iron to form a copper-iron sulfide matte which is separated from the slag. The matte is converted to metallic copper by oxidation to remove the iron and sulfur, and the copper is further refined to remove impurities (Turkdogan, 1983, Moore, 1981).

Copper smelting is done in bath processes and flash smelting furnaces with oxygen enrichment, but flash smelting is the predominant method practiced today (Peacey, 1989). The older reverberatory furnace practice has been described in the literature (Anderson, 1961, Fowler, 1961, Nicholson et al., 1961). Electric furnace smelting of copper sulfides has also been reported, and other smelting processes are being developed (Barth, 1961, Floyd et al, 1980, Phelps, 1991). In general, the slags in reverberatory furnace smelting, flash smelting, and other processes are similar. The Mitsubishi continuous smelting and refining process differs in that a calcium ferrite slag is used in the converting furnace.

Copper-bearing concentrates often contain 5 to 10% silica. About 5% additional silica is added as pure silica or ore, and the remainder of the silica is obtained from slag recycled from the converters used to make copper metal from the matte. Generally, lime in some form is added to break up silicates, take up excess silica from aluminosilicates, and reduce the viscosity of the silica-rich slag. Typically, 3 to 10% limestone or lime-bearing mix is added. A typical smelting slag contains about 30 to 45% FeO, 30 to 40% SiO_2 , 5 to 10% Al_2O_3, 2 to 6% CaO, and 2 to 4% MgO (Watanabe et al., 1980). The ratio of slag to metal varies but is often in the range 0.6 to 1.5.

One problem in recovering copper is the tendency to form magnetite in the converters, although a certain amount of magnetite

is required to attain high copper recoveries. Magnetite melts at a temperature higher than the temperature in either smelting or converting, has a low solubility in slags and matte, and doesn't form a silicate with the silica usually present in smelting because much of the silica is tied up in other forms. Typically, some free silica is added to tie up magnetite as iron silicate, but excess will react with basic furnace brick. The silica used is often of very high purity— greater than 90% SiO_2 (Fowler, 1961, Watanabe et al., 1980, Floyd et al., 1980). Although siliceous slags are usually used, it has been reported that lime-based slags compared to siliceous slags have a lower viscosity, a higher solubility for magnetite, separate easily from the matte, and are more efficient in removing arsenic, antimony, and bismuth (Turkdogan, 1983, Chaubal et al., 1989).

The size of flux must be compatible with the process, but in general the sizes used are the same as in ironmaking and steelmaking. In converters, the flux is in the range of 2.5 by 0.6 cm. Flux coarser than 2.5 cm is difficult to inject and to dissolve, and flux finer than 0.6 cm tends to float on the bath and is also a source of dust (Anderson, 1961). In the Sirosmelt process, the limestone used was 0.5 to 1.0 cm in size (Floyd, 1980).

Lead: Lead is processed by a number of older processes that include sintering followed by smelting in the lead blast furnace, electric furnace, or Imperial Smelting Process (ISP), and several newer direct and flash smelting methods such as Kivcet, Outokumpu, and QSL are being tried (Castle et al., 1989, Pickard and Crawford, 1989). In the blast furnace and ISP processes, lead sulfide ores are roasted to form lead oxide sinter which is charged with limestone and coke to the lead blast furnace or the Imperial Smelting Furnace (Moore, 1981). In the latter, lead is collected in the furnace bottom where it separates from slag, and zinc vapor exiting the top is condensed. In the direct and flash processing methods, the lead is partially or totally oxidized into the slag and the slag is treated in an electric furnace with carbon as coal or coke to reduce the oxidized lead to lead bullion (Turkdogan, 1983). Copper is removed from the lead by adding sulfur and by several other processes. Further refining is accomplished by oxidizing impurities with air, lead oxide, sodium hydroxide, or sodium nitrate flux and by electrorefining (Moore, 1981, Peacey, 1989).

Slags formed are complex. A typical lead blast furnace slag composition is: 2 to 12% ZnO, 20 to 25% FeO, 1 to 2% Fe_3O_4, 0 to 2% PbO, 16 to 19% CaO, 26 to 31% SiO_2, 5% MnO, 10% Al_2O_3, 1 to 2% CaS, and 5 to 10% MgO (Grant, 1980).

Nickel: Nickel ores occur as both sulfides and oxides. The sulfide ores often contain copper-iron sulfides in association with nickel-iron sulfides. For sulfide ores, the processing is accomplished by reverberatory or flash smelting furnaces and horizontal converters (Pickard and Crawford, 1989, Moore, 1981). Flash converting is being introduced (Phelps, 1991). Separation of copper and nickel sulfides from the matte is accomplished by crystallization, grinding, and froth flotation, and the copper and nickel sulfides are refined further. In nickel smelting from some ores, slag formation can be complex due to the presence of magnesia (MgO) in various silicate minerals. The slag is typically iron and silica rich, but with elevated magnesia levels. The magnesia will increase the melting point, and olivine $(Mg,Fe)SiO_2$ can crystallize out. This can be countered with silica and lime addition wherein lime decreases the viscosity of the melt (Davey et al., 1980).

In New Caledonia, an oxide ore comprising a nickel-bearing hydrated silicate of iron and magnesia containing 37% SiO_2, 2.2% Al_2O_3, 23% MgO, 20% Fe_2O_3, 2% Cr_2O_3, 0.3% CaO, and 2.2% Ni was sintered with gypsum ($CaSO_4 \cdot nH_2O$) and smelted in a blast furnace to an iron-nickel matte. This was further treated in a converter to remove iron (Thurneyssen et al., 1961, Habashi, 1986). At the now closed smelter at Riddle, OR, garnierite, a magnesium silicate containing alumina was smelted. The ore contained 25 to 38% MgO, 45 to 55% SiO_2, 1 to 3% Al_2O_3, 1 to 2% CaO, 8 to 15%

Fe, and 1.5% nickel (Ni). The Ugine process was used in which silicon as ferrosilicon (FeSi) was used as the reductant, and silica was formed in the process. Phosphorus was removed by oxidizing the bath with iron ore in the presence of a high lime slag. The metal was further refined with a slag containing lime and fluorspar (Coleman and Vedensky, 1961).

Tin: High grade tin oxide concentrate is smelted in reverberatory and electric furnaces, and low grade concentrate is smelted in blast furnaces, kilns, and horizontal furnaces (Castle et al., 1989). In the first stage of a two stage process, part of the oxide is reduced to metal with formation of a ferrous silicate slag containing a small amount of lime and unreduced tin as a tin silicate. First stage slags typically contain 30 to 40% SiO_2, 15 to 25% FeO, 5 to 15% CaO, and 5 to 25% SnO_2. In the second stage, the tin silicate is reduced by iron metal to form iron silicate and an impure tin which is recycled. Second stage slags from southeast asia typically contain 24 to 28% SiO_2, 9 to 11% Al_2O_3, 20 to 22% CaO, 12 to 20% FeO, 2–6% MgO, and impurity metals (Habashi, 1986).

ECONOMIC FACTORS

In industrialized nations, metal consumption per capita is thirty times that of underdeveloped nations (Anon., 1991a) and thus, the worldwide potential for increased metal production and the attendant flux consumption is very large. However, the rate at which demand will increase is not clear. World demand for metals and fluxes would be expected to be a function of population growth and economic growth, however, population growth is greatest in underdeveloped countries where economic resources are scarce. Whether reserves of metals will be sufficiently large to meet this potential demand is a subject of debate, however, it is clear that previously projected shortages are not yet developing (Castle et al., 1989). Fortunately flux minerals, and particularly limestone and silica, that would be required to support growth in metals consumption are abundant and widespread.

An excellent review of the state of the metals industry was recently published (Davis, 1989). This review suggests that consumption of both ferrous and nonferrous metals ceased growing around 1960, and in fact, has been negative recently. This is attributed to both the decreasing growth rates of the economies in industrialized countries and the decreasing intensity of metal use in both service industries and manufacturing. It has been proposed by several economists that the demand for raw materials has become uncoupled from economic growth (Davis, 1989). This is particularly true in Japan and the United States, and the impact has been greatest on the steel industry, the largest flux user. The implication of this trend is that economic recovery will not necessarily result in increased demand for metals (and hence fluxes). It is suggested that a period of new demand creation and market development will be required to stimulate further growth.

Recent changes in the Republic of South Africa and the new Commonwealth of Independent States (formerly the Union of Soviet Socialist Republics) and increased trade with China, will alter the supply and demand situation of certain minerals which could affect flux consumption. Greater imports of metals from these countries to the United States will impact domestic flux production and consumption. Even with increased imports of metals and other mineral commodities, it is not likely that any large scale trade in stone or silica flux will occur due to the abundance of sources, low value, and high transportation costs.

However, fluorspar, which is used at at rate of about 10 kg/t of steel is almost entirely imported to the United States because of high domestic production and transportation costs (Anon., 1991a). Metallurgical fluorspar imports and domestic consumption were about 110 kt in 1990. These imports were 70% from Mexico, 28% from China, and 2% from South Africa (Hodge, 1991). The latter is largely a low grade flotation concentrate for agglomeration into briquettes. The imports from China are increasing because Chinese fluorspar costs 50 to $60/t FOB port compared to Mexican fluorspar which is $90/t FOB port (Hodge, 1991). The demand for metallurgical-grade fluorspar is decreasing in steel and allied industries.

In both ferrous and nonferrous smelting processes, the trend to lower consumption of flux per unit of metal is due to economics resulting from an intense effort to reduce the quantity of slag formed which requires energy and to changes in smelting practices. The present deficiency of capital in the capital intensive metal industries has resulted in plant closures and consolidation in both the metals industries and the attendant flux suppliers. Alternative uses for limestone and dolomite previously used for fluxstone are being sought by producers.

GOVERNMENT CONSIDERATIONS

Government influences mineral and metal markets through labor laws, land use and environmental regulations, trade and energy policies, and funded programs and research. In the United States, the flux industry can be affected by actions of the Department of the Interior, Department of Energy, the Environmental Protection Agency, Occupational Safety and Health Administration, Mine Safety and Health Administration, and the Bureau of Land Management, to name a few.

The 1990 Amendment to the Clean Air Act will affect the domestic manufacture of coke which might drive the steel industry to conversion to scrap-based and premetallized burden electric furnace steel processing or coal-based direct ironmaking processes. Electric furnaces would require lower gangue feed stock, and hence would require less flux. Coal-based processes could require a change in the size requirement of flux used. Sinter plants presently making agglomerates from ores and steel plant wastes might be affected by these changes or environmental regulations in a way that will alter slightly the way in which flux is introduced to the blast furnaces.

Fluorspar imports and consumption were impacted by several recent actions. One was the September 1987 Montreal Protocol and the United Nations Environmental Program (revision), London, June 1990, in which chlorinated fluorocarbons (CFCs) and halons are to be restricted by the year 1995 and banned by the year 2000 (Hodge, 1991). In 1990, Mexican acid-grade fluorspar became eligible for preferential treatment, and a 13.5% tariff on imports of metallurgical-grade fluorspar was suspended through December 1992 (Anon., 1991a).

Mining and quarrying are industries that affect the environment, particularly the use of land. The stone industry in some instances has developed near populated areas which causes problems with dust, noise, blasting, trucking, etc. Little emphasis was placed on the environment in years past, however that has changed due both to increased awareness of the effects on the environment and to state and federal regulations. Environmental regulations that affect mining and quarrying are those that affect reclamation of process water and solid waste, reduction of dust and noise, and control of air and ground shock from blasting.

The Bureau of Land Management works under the Federal Land Policy and Management Act of 1976. This Act mandates that public lands be managed for multiple use (Anon., 1991a). This also requires that, following mining, land will be reclaimed for other uses. Other regulations of importance are those that affect use of wetlands and dunelands, revegetation of waste, and gradation of pit slopes. The Bureau of Land Management also administers mining on lands governed by the General Mining Law of 1872 (Anon.,

1991a). Recently, a study of the potential economic impact of repealing the General Mining Law was released (Anon., 1992). The study predicts that 30,000 jobs would be affected, and the cost to the federal government in lost revenues and expenditures would be several hundred million dollars annually.

For updates on minerals and land use planning and the General Mining Law, readers should contact the Bureau of Land Management. For further information on mineral statistics, minerals and the environment, recycling, or mining, readers should contact the United States Bureau of Mines.

PROBLEMS AND FUTURE TRENDS

In a low growth economic scenario, and with the demand for saving energy and improving the environment, the consumption of flux for metallurgical purposes is likely to continue downward. Metal production and flux consumption will be influenced by new process technologies, recycling, and substitution (Castle et al., 1989). Identifiable trends are the use of composite materials and lightweight materials in transportation vehicles, the increased use of high technology devices and miniaturization. Substitution of plastics, composites, and light alloys including aluminum will impact the use of steel and the attendant flux consumption; however, any increased use of aluminum will require some increase in fluorspar consumption. Space required for slag disposal and methods for containment of effluents from slag dumps to prevent transport of undesirable elements into the environment also drive lower flux usage.

Ironmaking and Steelmaking

Current blast furnace practice using domestic iron ore pellets with a nominal silica content of 5% requires a certain blast furnace slag practice that dictates flux consumption. Therefore, further reductions of flux consumed per ton of hot metal are not likely. Recently, there has been a trend to using fluxed pellets in the blast furnaces. In 1990, fluxed pellets comprised 34% of domestic production and the trend is increasing (Ranade, 1992). The use of fluxed pellets with flux from Michigan has displaced some flux used in sinter and, at some blast furnaces, flux from other sources. Presently, recycled steelmaking slag provides the additional flux needed by many furnaces. Sinter plants, although useful for recyling of steel plant wastes, could be closed for environmental reasons. There is also a trend to production of lower silicon hot metal and lower hot metal manganese requirements which results in lower flux consumption in steelmaking. Decreases in the consumption of lime and use of fluorspar in BOF steelmaking are also likely to continue.

Presently, there is overcapacity in the steel industry, and prices are weak (Anon., 1991a). Some steel mills are downsizing, and some are looking to alternative modes of operation. To achieve greater process throughputs, and higher quality steel, additional installations for external treatment of hot metal, particularly desulfurization will be built, more ladle metallurgy stations and vacuum degassing facilities will be installed, and scrap preheating for electric furnaces will be increased. The success of mini-mills, a desire by steel producers to decrease coke production to meet environmental regulations, and increased recycling of scrap is resulting in greater use of electric furnaces. According to a recent article, Karlis Kirsis of Paine Webber's World Steel Dynamics has projected that mini-mills will capture 14% of the domestic steel market in the year 2000, up from 6% today (Ashby, 1992). If major steel producers adopt mini-mill and electric furnace practices, the demand for lower silica iron sources is likely to increase, and a decrease in flux consumption is likely. Many iron and steel producers that once owned captive limestone and dolomite operations have sold them.

Over the last several years, there has been renewed interest in direct ironmaking and direct steelmaking processes. Direct ironmaking will very likely require a different slag practice than blast furnace ironmaking. New slag functions such as foaming to provide a blanket over the bath to achieve post combustion of gases and allow adequate heat transfer might redefine flux requirements. Both limestone and lime might be used in the same smelting vessel. The direct ironmaking processes will use coal in preference to coke which will increase the sulfur burden on the process. Use of coals of lower grade than present metallurgical coals might require alteration of flux practices.

It is well known that there is a trend to more recycling and reuse of wastes to protect the environment, and the steel industry is the single largest recycler of materials (Anon., 1991a). The reuse of steel saves iron ore, coal, limestone and dolomite flux, and energy. Byproduct slags have been used for landfill, ballast, aggregate, cement, and rock wool, and more uses for slag are needed.

Nonferrous Industry

Excellent reviews of the nonferrous industries in Europe and North America have been published recently (Castle et al., 1989, Pickard and Crawford, 1989). In the copper smelting industry, there has been considerable consolidation which has brought supply and demand more closely into balance, however, the relationship is tight due to disruptions in supply from foreign sources (Castle et al., 1989, Pickard and Crawford, 1989, Anon., 1991a). In copper smelting, there has been a trend to new technology development, with flash smelting and bath processes largely replacing reverberatory furnaces. Direct smelting using a lime flux has been proposed (Peacey, 1989). Flash converting is gaining in importance (Carter, 1990).

Copper is the third most consumed metal after iron and aluminum, and the greatest use for copper is in electrical applications (Anon., 1991a). Copper is affected by substitution, for example the use of plastic piping in domestic plumbing and the substitution of fiber optic cable for copper wire. The trend towards computerization and miniaturization, the development of lower voltage lighting systems allowing finer wire, lower power requirements of solid state devices, introduction of better magnet steels with lower power losses, and the development of high energy permanent magnets that allows development of smaller motors all could diminish the demand for copper. The effect of superconductivity on copper use is uncertain (Rieber, 1992). The known superconductors all contain copper, but wire will be smaller. However, the technology might spur some new industries and increase the demand for copper. There is an increasing demand for electronic shielding materials, and manufacture of all electric vehicles could increase demand for copper. Currently, 26% of copper production is from scrap (Phelps, 1991).

Lead is the fifth most produced metal after zinc, which is fourth (Castle et al., 1989). Lead smelting is likely to be adversely affected by the push for a lead-free environment which might lead to some decrease in flux consumption, however, demand for all electric vehicles could increase the demand for lead-acid batteries, the largest use for lead. A large portion of demand for lead is met by recycling, and this could increase in the future. Hydrometallurgical processing of lead ores might prove attractive in the future (Peacey, 1989).

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