OPTIMUM UTILIZATION OF BY-PRODUCTS IN THE FERROALLOY INDUSTRY

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ABSTRACT

Ferroalloy manufaturing operation involves generation of by-products such as slags, dusts, and gases. Particularly the slags are the largest in quantity produced, more than 1 million tons per year.

Currently in Japan, 90% of the ferroalloy slags are utilized in a number of applications. At our Takaoka plant, we have been able to achieve 100% utilization of not only the slags but also the dusts and gaseous by-products.

Manufacturers in the ferroalloy industry are actively promoting the optimum utilization of the slags. Today, it is used widely in such applications as fertilizers suitable for farming conditions and soil peculiar to Japan, refractories having excellent abrasion resistance and high temperature chemical resistance and heat insulation and other building materials.

It is likely that demand for slags will grow further for use as raw materials that imparts excellent features to various products.

INTRODUCTION

Japan is highly dependent on imports for most of the resources it requires. Therefore, the optimal utilization as well as stable supply of resources is a matter of utmost concern to the Japanese industry.

In the ferroalloy industry as well, it is one of the requirements to ensure stable supply and optimal utilization of resources along with energy cost reduction. As part of such efforts, researches have been carried on to realize recycling and regeneration of the by-products produced in ferroalloy manufacturing operation.

The bulk of the by-product slags, dusts, and gases are utilized in some forms of practical application. In particular the slags which are the largest in volume are used for a multitude of products that have been developed to date, ranging from roadbed material and fertilizers to more recent developments of high value-added functional materials. As demand for the quality of industrial materials becomes increasingly diversified in the broad areas of industrial application including new ceramics, we feel confident that products with higher added values can be developed through continued research and development efforts to meet emerging market needs.

This paper deals with the present status of our optimum utilization of ferroalloy by-products, mainly, slags.

PRODUCTION OF FERROALLOYS AND BY-PRODUCED SLAGS

Ferroalloy production in Japan totalled 1.42 million tons for 1984. As shown in Fig. 1, ferroalloy production for the past few years declined below 2 million tons/year due mainly to the slowdown in crude steel production, decreased consumption of ferroalloys in the steel industry, and increasing imports.

Although the by-product slags are on the decrease with a decline in ferroalloy production, it is still generated in a quantity of more than one million tons per year. Table 1 shows the quantity of main types of the slags generated in Japan. As can be seen from this Table, manganous slags are the largest in volume produced, accounting for 60 - 65%. The main reasons are that manganese alloys represent more than 50% of the total ferroalloy production in Japan and that the by-product slags with high concentrations of manganese are regenerated for use in manufacturing silicomanganese and other products.

Of the chromic slags, the low-carbon ferrochrome slag is much smaller in quantity at 70,000 - 80,000 tons because the metal production is at a level lower than 40,000 tons per year, though it is generated in a larger volume per ton of product, 2,000 - 2,200 kg.

Fig. 1 Ferroalloy Production in Japan

Table 1. Amount of Typical Ferroalloy By-Product Slags

(Unit: ton)

		1981	1982	1983	1984
Mn	H-C FeMn	371,754	285,550	231,325	259,794
	M, L-C FeMn	117,357	158,501	114,697	126,372
	Si-Mn	402,086	360,128	301,827	335,927
	Total	891,197	804,179	647,849	722,093
Cr	H-C FeCr	323,571	341,164	334,352	332,255
	L-C FeCr	92,542	71,342	76,887	83,812
	Total	416,113	412,506	411,239	416,067
Si	Fe-Si	16,650	20,772	17,253	11,234
	Ca-Si	1,684	2,463	1,682	1,214
	Total	18,334	23,185	18,935	12,448
	Grand Total	1,325,644	1,239,870	1,078,023	1,150,608

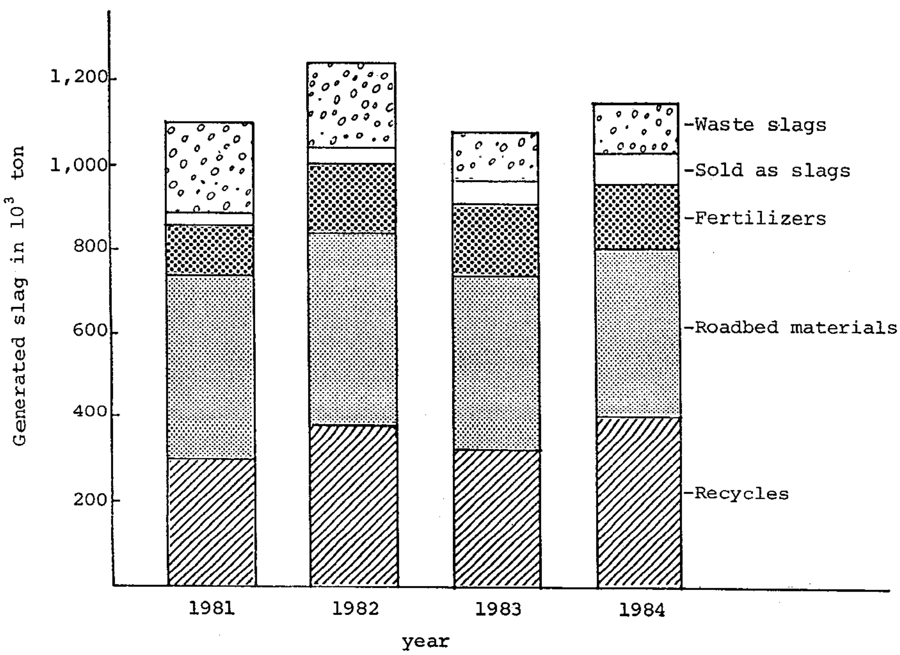
Source: Japan Ferroalloy Association

UTILIZATION OF FERROALLOY SLAGS

Since the effective use of ferroalloy slags lead to a cost reduction of ferroalloy products, manufacturers are putting positive efforts in their research for its optimum utilization.

The ratio of slag utilization including recycling, roadbed material, fertilizers, and those sold as slags were 79.5% of the total generated in 1981. Thereafter, it increased gradually over the following 4 years to 90.5% in 1984, with the volume of waste slags decreased to less than 10%.

The use of slags for products or as material of the products other than fertilizers and roadbed material also increased steadily to approx. 70,000 tons for 1984 and is estimated to exceed 100,000 tons, that is 10% of the total volume in 1986. Given in Fig.2 is a breakdown of slag utilization and in Table 2 is shown the uses of ferroalloy slags by types. Of the total manganous slags produced, 50% is recycled for ferroalloy production and approx. 20% is used in manufacturing fertilizer products. As much as 70% of chromic slags generated is sold for roadbed application but 17% is wasted, which is relatively a high ratio of waste. Silicon slags (ferrosilicon, calcium silicon slags) which are generated in a very small quantity, are utilized entirely as recycle material for ferroalloy production and for desulfurizing agent, among others.



Source: Japan Ferroalloy Association

Fig. 2 Utilization of Ferroalloy Slags

Table 2. Utilization of Ferroalloy Slags by Types (1984)

		Recycle	Roadbed	Ferti-lizers	Sold as Slag	Waste	Total
FeMn Slag	10^3t	395	98	147	40	42	722
	%	54.7	13.6	20.4	5.5	5.8	100
FeCr Slag	10^3t	15	295	13	23	70	416
	%	3.6	71.0	3.1	5.4	16.9	100
CaSi/FeSi Slag	10^3t	5	1	-	6	-	12
	%	41.7	8.3	-	50	-	100
Total	10^3t	415	394	160	69	112	1,150
	%	36.1	34.3	13.9	6.0	9.7	100

We are making every possible effort to make good use of the by-products from the viewpoint of optimal utilization of resources and cost reduction of ferroalloy products. At our Takaoka plant, we have achieved 100% utilization of the ferroalloy by-products.

Takaoka plant uses 300,000 tons/year of imported manganese ores to produce 200,000 tons of manganese ferroalloys including those for internal use. In addition, we manufacture and sell 100,000 tons/year of fertilizers. Of the ferroalloys, high-carbon ferromanganese is produced 60,000 tons/year, in which operation is generated 30,000 tons of by-product slag. The by-product slag which contains 25 - 30% manganese oxide (MnO) is consumed in its total quantity as raw material for low-carbon ferromanganese and silicomanganese. And, a total of 90,000 tons of the slag containing 5 - 10% MnO generated from silicomanganese, medium- and low-carbon ferromanganese production are sent to our fertilizer manufacturing plant. At the fertilizer plant are produced silicate, manganous, and fused phosphoric fertilizers. The slags that come from the ferroalloy plant are used as raw materials for various types of fertilizers manufactured at this plant. Some of the slags are used as raw materials for rock wool production which we started recently.

Dust collectors installed at our plant turn out a total of 8,000 tons/year of dry and wet dusts. All of the dusts are sent to a sintering plant which produces 130,000 tons/year of sintered ores for high-carbon ferromanganese and silicomanganese. Dry and wet dusts are mixed to adjust the water content, sintered with powdered ores and carbon material, and the sintered ore thus obtained is fed to an electric furnace for production of silicomanganese. Some 50% of the gas generated from the unit of two closed electric furnaces is sent to a adjacent subsidiary plant after removing dust by a Venturi scrubber and Theisen washer to be used as fuel for boilers. The remaining 50% is used as fuel for rotary kiln and dryers. As a source of energy, this gas with CO concentrations ranging from 50 to 70% provides a total of 100 million mega cal/year. Fig.3 shows a shcematic flow of by-product utilization at our Takaoka plant.

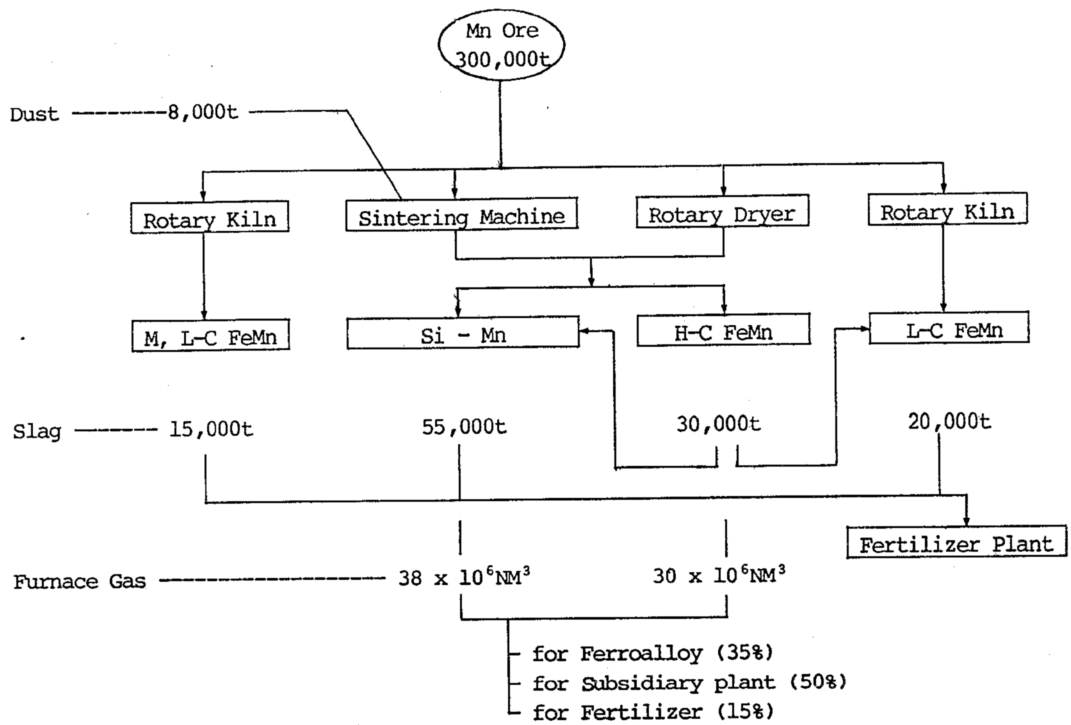


Fig. 3 Schematic Flow of By-Product Utilization at Takaoka Plant

Although all of the ferroalloy by-products are utilized at our Takaoka plant, we still have some unused slags that come from other plants of our overall ferroalloy operation and we feel it necessary to increase the value of such by-products now wasted. The following examples will illustrate the useful application of ferroalloy slags as experienced at our plant.

FERTILIZERS

Today in Japan, ferroalloy slags are used for silicate, manganous, and microelement composite fertilizers.

Silicate Fertilizer

In Japan, silicic acid which is a main component of silicate fertilizer is used in large quantities as an essential element for increasing the rice yield. Silicic acid is known to have an effect of reinforcing the epidermal cells of leaves, promoting sound growth and increasing the resistance against insects and diseases of rice plant.

The rice field area accounts for more than 40% of Japan's total cultivated area, representing a substantial portion of the demand for silicate fertilizer. Slags derived from ferromanganese, silicomanganese, and low-carbon ferrochrome are all permitted for use in silicate fertilizers under the Fertilizer Regulation Act. Table 3 shows standard specifications of silicate fertilizers and typical analytical values of the silicate fertilizer products that we sell.

We are selling two types of silicate fertilizers, consisting of slags from medium-carbon ferromanganese, low-carbon ferromanganese, and low-carbon ferrochrome. These products are supplied in two different particle sizes to meet specific requirements of users, one is water-milled and dried into sand-like grains and the other is ball-milled and pelletized after addition of binder.

Table 3. Standard Specifications and Analytical Values of Silicate Fertilizer Components (%)

		S-SiO_2	CaO+1.4MgO	C-MgO	C-MnO
Standards	(I)	$\geq$20	$\geq$35	-	-
	(II)	$\geq$20	$\geq$30	$\geq$1	-
	(III)	$\geq$20	$\geq$30	-	$\geq$1
	(IV)	$\geq$20	$\geq$30	$\geq$1	$\geq$1
Analytical	(II)	25.1	60.8	9.2	-
values	(IV)	36.5	40.1	3.8	6.2

Note: S : soluble in 1/2 N HCl
C : soluble in 2% citric acid

Manganous Fertilizer

Among the microelements contained in the plants, manganese is the largest in quantity and is considered as one of the elements essential for plant growth. A trace amount of manganese added to fertilizers is known to produce an effect of accelerating the growth of rice plant and other crops. It is also said that in some kinds of vegetation, the deficiency of manganese cannot be remedied by any other elements.

In our operation for manufacturing silicomanganese products, we use such additives as dolomite and serpentine as fluxes and the slag resulting from the production is used as principal raw material for manganous fertilizers. This type of fertilizers contains citric acid-soluble MnO in the amount of 10%, which is a component required under the established standards. In addition, it contains other auxiliary ingredients, SiO (40%), CaO, and MgO, which makes it useful also as a soil improver for general use. Table 4 shows the standard specifications of manganous fertilizer components and typical analytical values of our products.

Originally the product was sold in powder but is now supplied as pellets, 3 - 5 mm in size, to prevent excess scattering in use. In the case of pelletized product, the composition of ingredients and the amount of binder to be added are adjusted in the process of slag preparation and pelletization, so that the pellets will disintegrate only gradually over an extended period of time, thus exhibiting a sustained fertilizing effect.

Table 4. Standard Specifications of Mn Fertilizer and Analytical Values (%)

	C-MnO	S-MgO	S-SiO_2	S-CaO
Standardds	$\geq$10	-	-	-
Analytical values	10.5	6.5	40.2	28.5

Microelement Composite Fertilizer

The type of fertilizers warranted to contain manganese and boron among other elements that are recognized in Japan as essential microelements, is generally referred to as microelement composite fertilizer. We manufacture the product by blending ferromanganese slag with colemanite and dissolving the compound in an electric furnace. Table 5 shows the standard specifications of the components of microelement composite fertilizers and typical analytical values.

Table 5. Standard Specifications of Microelement Composite Fertilizers and Analytical Values (%)

	C-MnO	C-B_2O_3	SiO_2	CaO
Standards	$\geq$10	$\geq$5	-	-
Analytical values	15.1	7.4	27.4	40.5

We also manufacture fused phosphoric fertilizers, one of which contains citric-acid-soluble MnO in the amount of 3% and is sold as soluble microelement composite fertilizer. Still other products that we sell include mixed fertilizer which is a combination of phosphoric and silicate fertilizers blended in a certain ratio, and home gardening fertilizer consisting mainly of silicate material. Since Japan is limited in its arable land, fertilizers play an important role in improving agricultural productivity. As mentioned earlier, ferroalloy slags are utilized effectively in Japan not only for silicate fertilizer but also as raw material for microelement and composite fertilizer products. We feel that ferroalloy slags will find continued use as an essential material in producing fertilizers that best suit the specific conditions of local farmland and types of crops cultivated.

REFRACTORIES

With the advance of industrial technology, demand is growing for refractories and products capable of standing use under severe conditions. In this field, research is being conducted actively for new refractories that offer unique characteristics superior to conventional products.

Ferroalloy slags contain a high percentage of mineral ingredients like MgO, Al_2O_3, and SiO_2 which are suitable for refractoties. By making the most of this feature, we manufacture refractories.

Abrasion Resistant Castable Refractories

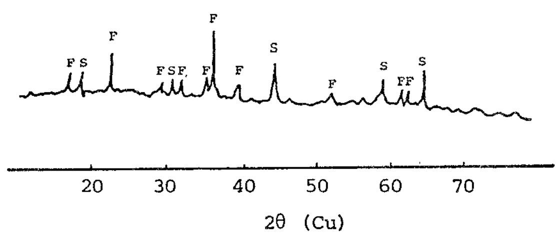
Chamotte is used as aggregate for most of the castable refractories available today for use under intermediate temperature condition, ranging from 450 to 1,350°C. Such chamotte-based castable refractories are not quite statisfactory in terms of abrasion resistance. While the high-carbon ferrochrome slag has good abrasion resistance, we are making use of this characteristic feature of the slag, instead of chamotte, as aggregate in manufacturing castable refractories for use in the intermediate temperature region.

The high-carbon ferrochrome slag comprises forsterite, spinel, and vitreous matter (10 - 15%). Table 6 shows the chemical components of high-carbon ferrochrome slag and, in Fig.4, its x-ray diffraction pattern. The Mohs hardness of this slag determined by comparison with mineral specimens is 7 - 8, which is equivalent to granite and limestone, much higher in hardness than chamotte, and is highly suitable for aggregate application requiring abrasion resistance.

The slag readily forms a solid solution with alumina-cement, alumina- or silica-based fine powder materials used as binder. Therefore, when used as aggregate, it provides as much strength as does chamotte to the joint between the aggregate and binder. While chamotte has a drawback of unsatisfactory abrasion resistance, the use of high-carbon ferrochrome slag makes it possible to manufacture castables with superior performance in this respect.

Table 6. Chemical Components of High-carbon Ferrochrome Slag (%)

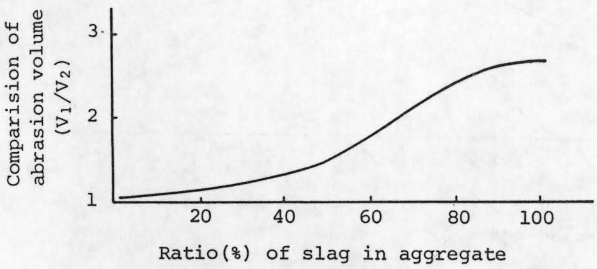
Cr_2O_3	SiO_2	CaO	Al_2O_3	MgO
2-5	25-35	5-15	23-30	25-35



F: Forsterite ($SiO_2 \cdot 2MgO$)
S: Spinel (mainly $MgO \cdot Al_2O_3$)

Fig.4 X-ray Diffraction Pattern of High-carbon Ferrochrome Slag

Fig.5 shows the results of abrasion resistance test conducted with a castable refractory comprising chamotte and alumina-cement in a ratio of 80 to 20% respectively, and a castable refractory with the aggregate replaced by high-carbon ferrochrome slag. The test specimens were exposed to a jet of 20 mesh SiC particles at 1,000°C, 30 m/sec. It can be seen from this test result, the use of high-carbon ferrochrome slag brings about conspicuously improved abrasion resistance.



V_1 : Abrasion volume when chamotte was used for aggregate

V_2 : Abrasion volume when slag was substituted for chamotte

Fig.5 Abrasion Resistance Test on Castable Refractory Compounded with High-carbon Ferrochrome Slag (%)

Informations we received from users of our slag-containing castable refractories, also support this test result in that the life of the castable, they describe, is three times as long as that of chamotte-compounded castable.

Castable Refractories for High-Temperature Application

We manufacture ferroalloy products also by aluminothermit. The slag generated in this operation has a high content of Al_2O_3 in a ratio of more than 80%, coupled with the refractoriness being higher than SK39. By virtue of these characteristics, the slag is highly suitable for use as raw material of high-Al_2O_3 castable refractories for high-temperature application. The type of castable for high-temperature application, up to 1,700°C, that we are now manufacturing and marketing, have been developed after a series of tests on the particle composition of ball-milled thermit slag and various combinations of cement binders. The characteristics of this castable is shown in Table 7 and its expansion and contraction curves are given in Fig. 6.

Table 7. Characteristics of Thermit Slag-Containing Castable

Max. Temp	Chemical Composition SiO_2	Chemical Composition Al_2O_3	Compression Strength kg/cm^2 at 1,450°C	Bending Strength kg/cm^2 at 1,450°C
1,700°C	4	82	450	115

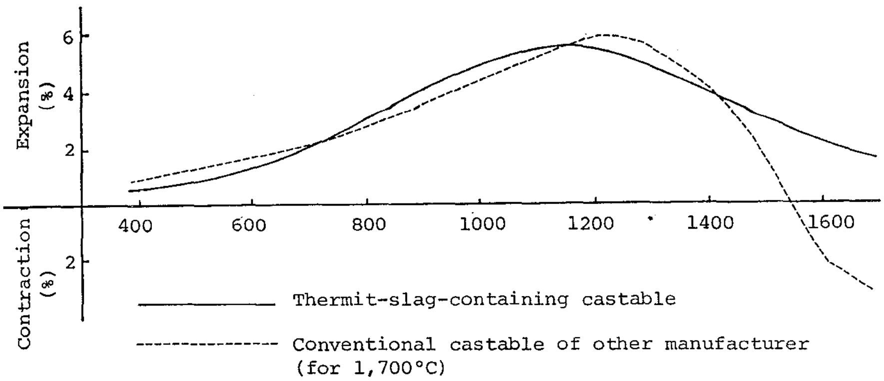


Fig. 6 Expansion and Contraction Curves of Castable Refractory

As is evident from Fig. 6, the use of alumino-thermit slag makes it possible to manufacture excellent castables with lower expansion and contraction at high temperature as compared with conventional castables for high-temperature application. Very good results of performance have also been obtained from its application used for high temperature spot 1,600 - 1,700°C.

ROCK WOOL

Rock wool is manufactured by melting the raw material that consists mainly of CaO and SiO , and fibrillating it either by blowing with compressed air or centrifuging with a high-speed rotor.

Rock wool is an amorphous matter inherently incombustible, lightweight, excellent in heat insulating properties, and highly durable. Because of these features, it is used widely as heat insulating material for building and plant facilities, and as fire-preventive and fire resistant material for buildings. In Japan, steel manufacturers have been producing rock wool for years from blast furnace slag as major raw material. For rock wool manufacturing, either silicomanganese slag or low-carbon ferromanganese slag is generally used as raw material. In our factory, we manufacture rock wool for lagging material application, using low-carbon ferromanganese slag. Table 8 shows the characteristics of our rock wool product.

Table 8. Characteristic Values of Rock Wool

Density (kg/m^3)	Fiber Thickness (μm)	Particle Content (%)	Thermal Conductivity (Kcal/m.h.°C)
110-130	3-5	2-3	0.031-0.035

SILICA FUME

Silica fume is a powdery substance of extremely fine particle size, with a high SiO_2 content (90%), which is generated in ferrosilicon and metalic silicon manufacturing operation. Silica fume is used in a wide range of application. It is characterized in that SiO contained therein is mostly in its amorphous state after being cooled rapidly following oxidization in the air of SiO generated at high temperature and that it consists of fine particles with specific surface area of 20 - 25 m^2/g which is twice as large as that of cigarette smoke particles. The chemical components of our silica fume product are shown in Table 9 and its x-ray diffraction pattern in Fig. 7.

Table 9. Chemical Components of Silica Fume (%)

SiO_2	Al_2O_3	Fe_2O_3	CaO	C
88-94	0.3-1.2	0.5-2.0	0.2-0.6	0.9-1.8

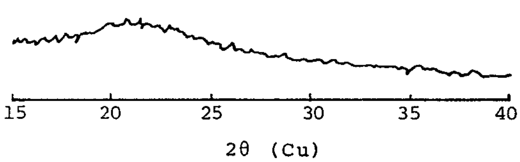


Fig. 7 X-ray Diffraction Pattern of Silica Fume

Silica fume is known to have an excellent effect when used as a concrete compound. SiO in its amorphous state in silica fume, bonds with calcium hydroxide that results from liberation in the hydration reaction of cement to form silica lime hydrate. In this process, a high pozzolan effect is produced, thus making it possible to increase the strength of cement. This is attributable to the characteristically high content of amorphous SiO and the large specific area of silica fume particles. Silica fume being extremely fine particles, it fills up fine pores in cement, which is another feature of silica fume that adds to the marked improvement of cement strength and durability. It is also known that the addition of silica fume to cement compound greatly enhances the electrical resistance of concrete and produces a high effect of preventing reinforcement bars from rusting. Other applications of silica fume include building material, refractories, and binders. In consideration of its varied applications, we optimize the particle size and product quality by application, so as to improve the ease of its handling and transportation and to meet specific requirements of users.

OTHER APPLICATIONS

In addition to these examples of optimum utilization, the ferroalloy slag offers many other potential uses in developing products having excellent properties; for example raw material for high strength concrete, compounded with low-carbon ferrochrome or SiMn slags; calcium silicate board comprising a combination of low-carbon ferrochrome slag and silica fume as principal raw material; and calcium slag additives for castings. It is further known that for decorative articles and decorative building materials having superb properties of color and hardness, ferrochrome and silicomanganese slags can be used as raw material after making adjustment of its composition and heat treating it with addition of oxides such as chrome, copper, and manganese.

Ferroalloy slag is generated under melting conditions at high temperature and it contains practically no alkali compound such as K and Na and halogenated compound such as chroline and fluorine. Its crystalinity can be adjusted to some extent by changing cooling conditions. For the purpose of meeting emerging demand for finely powdered raw materials that improve the quality of industrial materials, some types of slag like ferromanganese slag and low-carbon ferrochrome slag can be processed into fine particles of several microns in size by adjusting cooling conditions and causing disintegration by taking advantage of changes in volume that occur in the process of transformation of crystals. It is most likely that these types of slag and silica fume will find their way into broader areas of application as new materials.

CONCLUSION

As viewed from the standpoint of optimum application, ferroalloy slag currently finds a greater demand in the field of fertilizers and its application to refractories and building materials is increasing steadily. In Japan, manufacturers are working actively towards practical application of ferroalloy slags in many areas. Within the Japan Ferroalloy Association organized by ferroalloy manufacturers, we have a slag research committee which is carrying on joint research programs and publicity activity, disseminating relevent information to users. In view of the diversifying needs for industrial materials of varied types and properties, it is our intention to continue working for development of higher-value-added slag materials in our ongoing research in close cooperation with users.

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