The influence of lime and synthetic lime products on steel production

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SYNOPSIS

The importance of the chemical and physical properties of lime has been overlooked for years although the quality of lime plays an important role in the production of steel. With the introduction of the oxygen injection process these properties have been re-evaluated. The CaO, MgO, S, and P_2O_5 contents of lime are important, but so are the physical properties such as granulation, reactivity with respect to slag formation, and the degree of burning. Soft burnt lime enhances de-phosphorisation and de-sulphurisation, and facilitates the smelting process in general, mainly due to its large specific surface. Special lime, prepared as briquettes from quick-lime and fluxes or as pellets from limestone and various fluxes with or without binding agents, clearly accelerates lime dissolution during the slag formation process, lowers the melting point, and enhances de-phosphorisation, de-sulphurisation, and de-carburisation even more than soft burnt lime. The introduction of special limes in the oxygen injection process for steel production has opened up new fields for commercial exploitation of slags as well as improved operational techniques.

SINOPSIS

Die belangrikheid van die chemiese en fisiese eienskappe van kalk was vir 'n lang tyd verontagsaam alhoewel hierdie eienskappe 'n belangrike rol speel in die produksie van staal. Met die koms van die suurstof verrykings proses, was 'n herwaardasie gemaak van die eienskappe van kalk. Bestanddele soos CaO, MgO, S en P_2O_5 in die samestelling is belangrik, maar so ook die fisiese eienskappe soos byvoorbeeld korrelagtigheid, reaksie vermoë met betrekking tot slak vorming, asook die graad van verbranding. Sagte gebrande kalk bevorder ont-fosforisering en ontswaweling asook die smeltings proses in geheel asgevolg van sy groot spesifieke opper-vlakte. Spesiale kalk, wat van ongebluste kalk en sekere smeltmiddels in briket vorm asook kalksteen en ver-skeie smeltmiddels in korrel vorm met of sonder verbindings-stowwe gemaak word, bespoedig sonder twyfel die oplosbaarheid van kalk in die slak vormings proses, verlaag die smeltpunt van die slak, en bevorder ont-fosforisering, ontswaweling en ontkoling van staal tot 'n groter mate as sagte gebrande kalk. Met die byvoeging van spesiale kalk tot die suurstof verrykings proses in staal produksie het daar nuwe deure oopgegaan vir kommersiële aanwending van slak asook vir vindingrykheid in produksie tegnieke.

INTRODUCTION

Lime as a basic flux in steel production plays an important role in the sequence of metallurgical re-actions. It is therefore, surprising that its properties have not been more fully investigated for nearly a hundred years. The tests used went no further than the determination of the chemical analysis, although considerable doubts still existed with respect to the contents of magnesium oxide and sulphur. Metallurgical lime in the Fifties, in a number of smelting plants, consisted of a mixture of particles of all sizes from very coarse to very fine, with additional components such as silicon dioxide and sulphur concentrated in the fine particles.

Before the introduction of the oxygen injection process, attempts were made to improve the procedure in the bottom-blowing converter, and greater attention was paid to the lime quality, i.e., the chemical composition, the granulation and, since 1953, to the reactivity, especially the degree of burning of the lime. Much work has been done on the significance of the lime quality required for the metallurgy of the Siemens-Martin and Thomas processes. The lime quality was obviously less important for the Siemens-Martin process with a smelting period of 6 to 8 hours, than for the process with blowing periods of 20 to 25 minutes. It was due to the introduction of the oxygen injection process, that attention was directed to the properties of lime.

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CHEMICAL COMPOSITION

Great importance is attached to the calcium oxide content of the lime, this being about 95 per cent under present conditions. The content of carbon dioxide should be as low as possible, which is important for the heat balance and for quiet injection conditions. The upper limit for soft burnt rotary kiln lime is 1,5 per cent CO_2 depending on the degree of burning. The MgO content of lime is of increasing importance. The favourable influence of a dolomite lime addition on the refractory lining life is often mentioned, though this has not as yet been applied in Germany. Fundamental laboratory experiments have proved that this is so, but it was found at the same time, that the MgO contents must be kept sufficiently low to ensure that the satura-tion limit of magnesium oxide, with its disadvantageous consequences, will not be exceeded. The metallurgical lime, used for oxygen injection processes in Germany, with a magnesium oxide content of 1 to 2 per cent, meets most of these requirements.

The sulphur content of the lime, which limits the de-sulphurisation according to Schleicher, Lutz and Graven-horst, is important in steel production. Under certain circumstances it may result in an increasing re-sulphur-isation of the steel. The sulphur content in lime is of great importance for soft and low-manganese steel. If it is reduced by 0,1 per cent, the sulphur content in steel is reduced by approximately 0,005 per cent. As the sulphur content in scrap fluctuates considerably according to the kind of material and is in general unknown, the steel producer tries to obtain favourable metallurgical results by low sulphur content in lime, although this is

generally low compared with that in scrap and pig iron. The sulphur content in lime depends on the kind of fuel used for lime burning, the kiln aggregate and the burning conditions. In Germany, it lies between 0,06 per cent and 0,09 per cent for coke-heated shaft kilns and, in the case of natural gas-heated rotary tubular kilns, below 0,02 per cent.

PARTICLE SIZE

It has been found that different procedures require lime of different grain sizes. Lump lime between 8 and 40 mm is used in the oxygen injection process for steel, whereas a couple of companies in the same field prefer a more homogenous granulation. In general it is found that the sub-grain should not exceed approximately 10 to 20 per cent and that the fines, which would favour formation of accretions, are limited. The maximum content of fines is approximately 4 per cent.

REACTIVITY

Although opinions on the analysis and the size range

conform with each other, we find varying results with respect to the influence of the lime reactivity on the slag formation during the oxygen injection process.

Special attention has been paid to soft burnt lime, which has a large specific surface and a good reactivity with respect to the slag formation. In Fig. 1 a comparison is made of oarse grain titration, wet quenching curve and microstructure of soft burnt lime with those of other kinds of lime. These are important factors for the determination of the lime quality. The large specific surface should have a favourable effect on the metallurgical reactions.

According to Behrens, Koenitzer and Kootz, soft burnt lime favours de-phosphorisation and de-sulphurisation, and facilitates the smelting process with reduced splitting. The sulphur distribution (Fig. 2) between bath and slag is, in the final analysis, better with soft burnt lime than with hard burnt lime in smelting processes using slags of the same basicity. The same applies to a lesser degree for the de-phosphorisation (Fig. 3). Also in this case, especially with low iron oxide contents in the slag, the phosphorus contents in the steel are reduced by the use of soft burnt lime. Furthermore, it was possible to reduce the lime quantity by approximately 15 per cent and to increase the output of steel by 1 per cent. A reduced feed of lime permits larger quantities of scrap to be used.
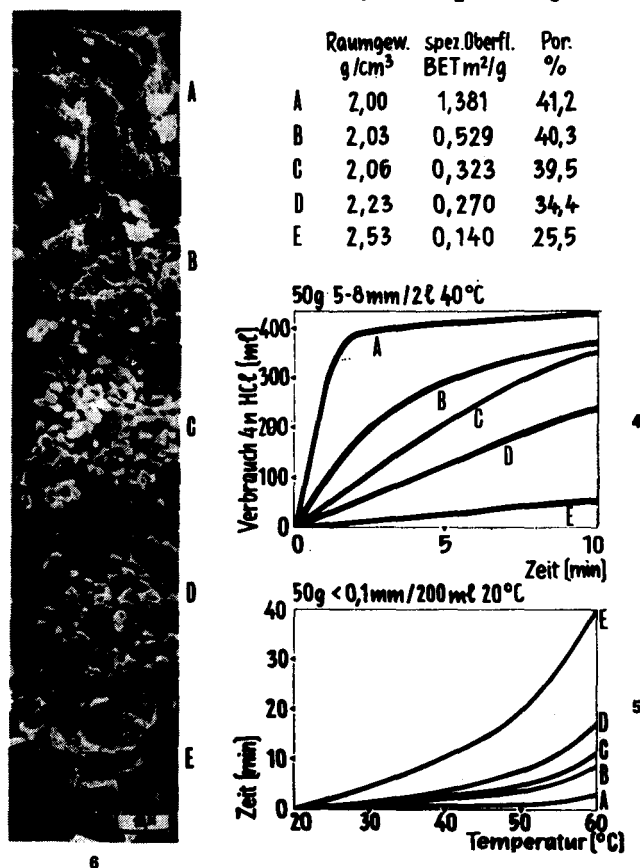

	1	2	3
	Raumgew. g/cm³	spez.Oberfl. BET m²/g	Por. %
A	2,00	1,381	41,2
B	2,03	0,529	40,3
C	2,06	0,323	39,5
D	2,23	0,270	34,4
E	2,53	0,140	25,5

Fig. 1—Properties of burnt lime containing 0,08 % residial CO₂
1. Specific gravity.
2. Specific surface.
3. Porosity.
4. Coarse grain titration.
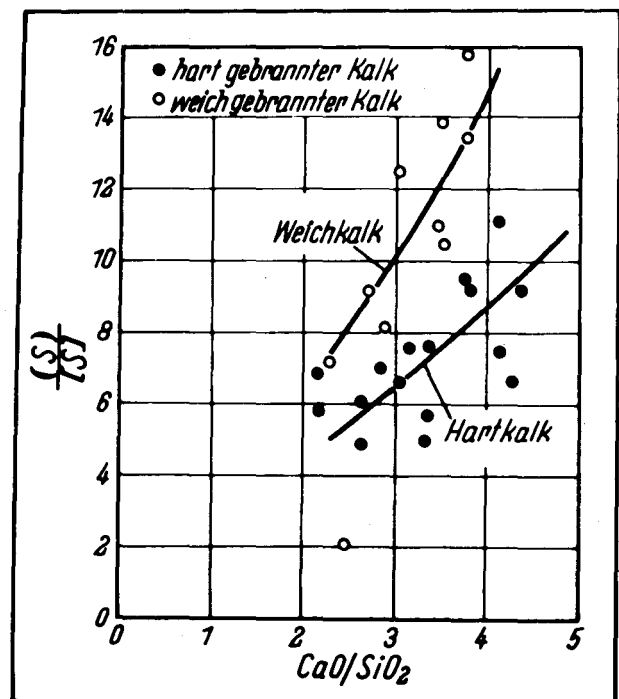5. Wet Quenching curve.
6. Microstructure.

Fig. 2—Sulphur distribution between bath and slag in steel smelting
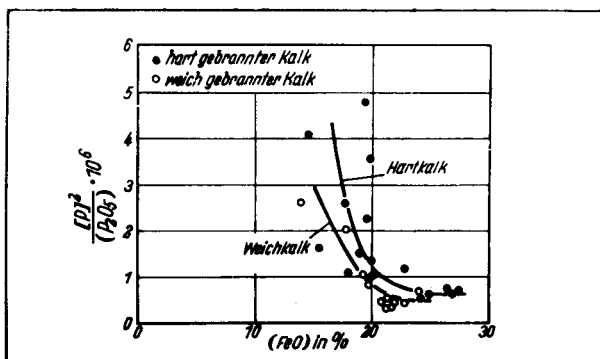● Hard burnt lime.
O Soft burnt lime.

Fig. 3—Phosphorous distribution between bath and slag in steel smelting.
● Hard burnt lime.
O Soft burnt lime.

LIME IN THE BASIC OXYGEN PROCESS

The opinion that soft burnt lime offers advantages in the basic oxygen smelting process is only partly confirmed and generally not accepted. For fine lime, this can be explained by the fact that the discrepancies in the properties of lime due to different burning degrees decrease with increased grinding fineness and should theoretically disappear at the size of the crystallite. This has been confirmed by plant experiments. So far, it has not been possible to explain the different opinions on the influence of the lime reactivity regarding lump lime.

Our tests yielded an explanation for the varying results in using soft burnt lime. In the laboratory we have conducted experiments with a view to changing the burning degree of the lime during the short blowing periods. If a critical value, which is determined by temperature and time, was exceeded, the soft burnt lime was found to overburn and the reactivity was reduced due to an accretive crystallisation (Fig. 4). The original soft burnt lime has only half the reactivity when heated to a temperature of 1 600 °C and an over-burning time of 3 to 5 minutes; after 10 minutes it becomes even less reactive.

These results were tested in two oxygen injection steel works. In Plant A steel with a low carbon content is produced by decarburising within a short time at comparatively low temperatures. For the production of steel with a higher carbon content plant B has to retard the decarburisation by an interceptive smelting process. This causes a rapid rise in temperature. In Fig. 5 a comparison may be made of the temperature run during the different smelting processes of plants A and B. Stereoscan exposures of lime samples taken from the converter are also shown. It can be seen that in the smelting process, during which the temperature is kept low for a considerable time (1 400 °C is not exceeded during the first 70 per cent of the blowing period; thereafter however, the temperature rises considerably), the lime does not overburn. The advantages of soft burnt lime can therefore be fully used. The advantages do not appear in the other procedure, as the fast rise of temperature in the bath and slag causes over-burning of the lime. This explains why, through experience, plant A is very successful in operations with soft burnt lime, whilst plant B obtained anomalous results and does not

in general use soft burnt lime. There are two opposing processes when the soft burnt lime is added to the con-
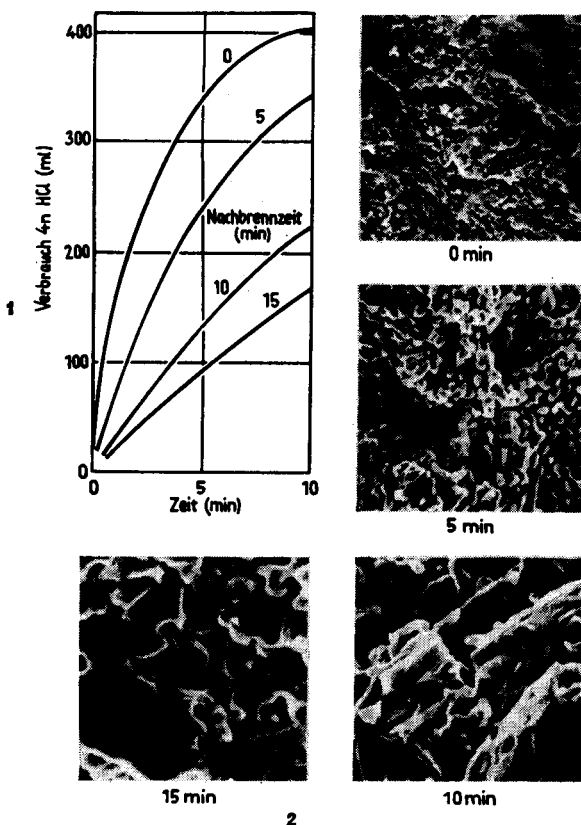

Fig. 4—Overburning of soft burnt lime
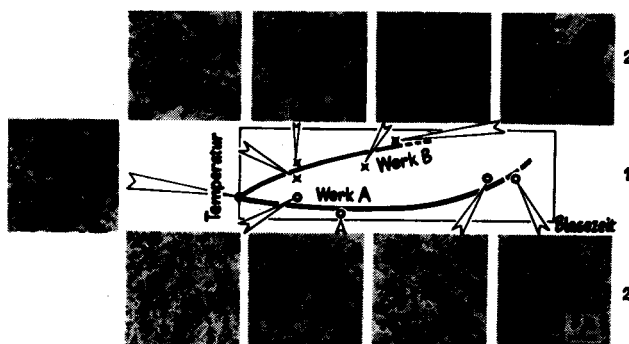1. Coarse grain titration.
2. Microstructure.

Fig. 5—Influence of temperature on the morphology of lime
1. Blowing Time.
2. Stereoscan of lime.

verter, viz., the rate at which lime dissolves in the slag and that at which the lime becomes overburnt. It is advantageous if the rate of dissolution of the soft burnt lime is faster than the rate of over-burning. A fast over-burning lime reacts like a low reactive lime.

SKIN-COATING OF LIME

There is, however, another often discussed effect which counteracts the dissolution of the lime. In the basic oxygen procedure, the reaction of the initially produced ferro-manganese silicates with the lime,

results in the formation of a high-melting dicalcium silicate which may also cause coatings and thereby disturb the dissolution of the lime. Fig. 6 gives an example of such a phenomenon. (It shows the dicalcium silicate skin around the lime core, as well as the remaining silicate coating on the slag.) The dicalcium silicate skin, through the channels of which Fe^{2+} ions are diffused from the slag into the lime and Ca^{2+} ions are transported into the slag, does not directly adhere to the surface of the lime, but is separated from it by an oxide skin and very often by a tricalcium silicate skin as well·

These skins have been examined with a microprobe and it was found that the dicalcium silicate which is situated around the lime core, and behind that the oxygen skin causing the mass transport, is a complex mixed crystal of dicalcium-tricalcium phosphate in which calcium is replaced by iron and manganese, and the silicon dioxide partly by phosphoric acid.
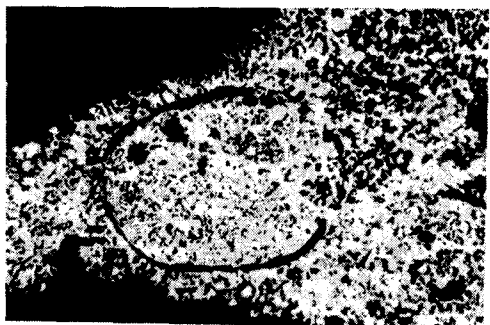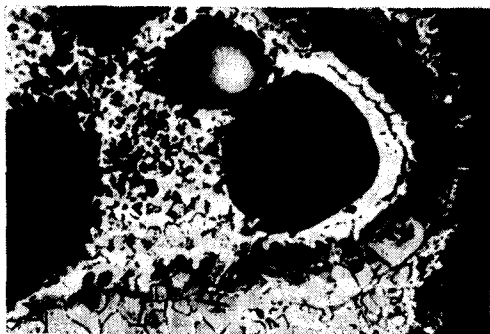

Fig. 6—Dicalcium silicate coating on lime

Silico-phosphates are formed during the oxygen injection treatment of phosphor-rich pig-iron. The protoxide skin consists of calcium-iron-manganese oxide mixed crystals. Using the microprobe, quantitative measurements have been made on lime in the process of dissolution and it was found that — according to fundamental experiments on the dissolution of lime — the lime mixed crystal in the $CaO\text{-}FeO_n$ system builds up to saturation and then melts. This is also valid for all other steel making processes. As the dicalcium silicate formation counteracts the dissolution of lime, it favours overburning and is therefore even more disadvantageous. Fundamental experiments have proved that in a pure four component system $FeO_n — CaO — SiO_2 — P_2O_5$, a silicate-phosphate barrier is present in the phase system even at very low P_2O_5 contents, so that it must be taken

into consideration in steel iron slags. The question arises whether soft burnt lime, which already offers many advantages compared with the standard lime, represents the optimum, or whether the lime can be further improved in order to optimize the oxygen injection procedure.

Any such improvement, as already stated, should in the first place result in promoting the dissolution of lime by influencing the dicalcium silicate formation by anticipating the formation of the mixed crystal, and thereby retarding the over-burning. In order to influence the formation of the dicalcium silicate skin, it is necessary to minimize the saturation surface of the dicalcium silicate in the phase diagram, or to repress it to lower temperatures, or at least to influence the segregations (such as thick skins and islands).

EFFECT OF FLUXES ON LIME DISSOLUTION

It is already known from the study of phase diagrams, that compared with the aforementioned phosphoric acid, fluxes of manganese oxide and magnesium oxide repress the saturation range of the dicalcium silicate in the $CaO\text{-}FeO\text{-}SiO_2$ system. Fig. 7 shows the reduction of the melting temperature of dicalcium silicate by several fluxes as may be deduced from the ternary phase diagrams $CaO\text{-}SiO_2\text{-}X$ in 'Phase Diagrams for Ceramists'. It is shown that pure iron oxides are more effective than dicalcium ferrite; and yet alumina, fluorspar and borate are still more effective. The borates in particular will be dealt with at a later stage. Adequate fluxes for the proposed special lime are in the first place oxides from the first to the third group of the periodic system as well as their combinations which have the tendency to displace the dicalcium silicate saturation range, to influence the formation of the dicalcium silicate, to reduce the CaO fusion point, and furthermore to retard or even suppress over-burning of lime. In order to verify these ideas laboratory tests have been carried out to determine the dissolution sequence of the special lime
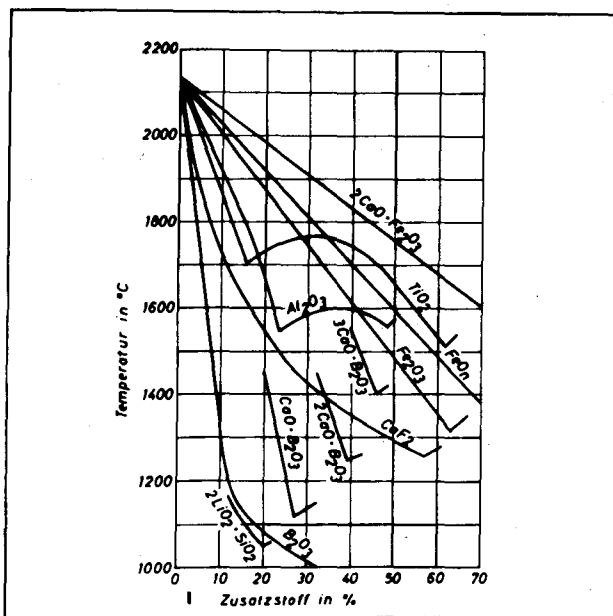

Fig. 7—Reduction of melting point of $2CaO.SiO_2$
1. Flux %.

hen pressed into cylinders of fine lime and flux. The lower broken curve in Fig. 8 represents the dissolution of soft burnt lime. A considerable improvement can be obtained by adding oxide slurry and further advantages are offered by the use of alumina carriers.
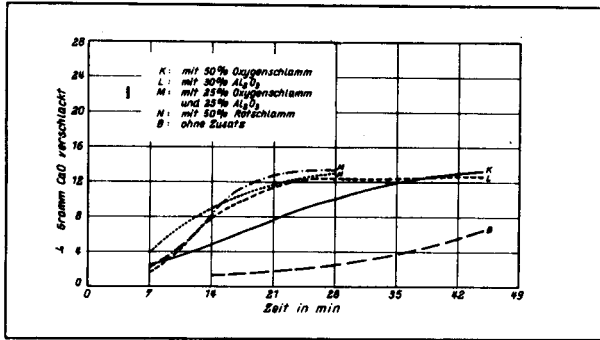

Fig. 8—Dissolution of soft burnt lime mixed with fluxes

1. **K: With 50% oxide slurry**
   L: With 30% AL₂O₃
   M: With 25% Al₂O₃
   N: With 50% red slurry
   B: Without flux

2. **CaO dissolved.**

SPECIAL LIME BRIQUETTES

According to Lellep, the use of special lime in the steel plants should make it possible — due to the regular distribution of fluxes — to reach an effect which is similar to that of preformed slag. The fluxes required for the special lime, which according to our present knowledge are required in addition to the soft burnt lime, may either be included in the naturally occurring limestone deposits — a rather rare occurrence — or may be added to the limestone during the lime burning operation. For the Siemens-Martin and electric arc furnace procedures, but particularly for the slag treatment after tapping, a number of possibilities have been discussed and tested. Our particular work has been in the briquetting of quicklime and fluxes and the pelletizing of limestone meal and fluxes.

Finely ground material must be aggregated by the production of briquettes as powdered material can be injected by a lance into the electric furnace, but cannot be used in the basic oxygen converter due to the high oxygen injection rates. The exhaust gas also carries off too much of the fine material which causes difficulties in the boiler and dust cleaning plants.

Not all kinds of quicklime can be pressed into briquettes of sufficient consistency without a binding agent as some of them show a great tendency for re-expansion. Unfortunately, this seems to be the case with our Devonian lime deposit. The quantity and distribution of the silicic acid seem to be of some importance. For the briquetting with a binding agent, it has to be noted that the binding agent should be dehydrated and desulphurised as steel manufacturers pay special attention to the sulphur contents. The briquettes are of uniform size which is very favourable for the whole process. If we compare these briquettes with the lime

used in the Fifties, we will recognise the development that has occurred during the last ten years. The briquettes are most effective if they decompose as fast as possible on addition to the slag in order to offer a large surface for dissolution. Such a decomposition can be caused by certain kinds of additives such as gas-splitting substances or temperature sensitive substances.

The pellets made of limestone meal and flux are dried and burnt, requiring a high burning temperature for a complete de-acidification. As we use rotary tubular kilns with Lepol preheaters, the pellets produced should not only have a sufficient initial strength, but should also be resistant to impact and attrition at temperatures between 600 and 800 °C. Within this temperature range the pellets are fed from the Lepol grate into the rotary tubular kiln. Such pellets can be made from appropriate combinations of binding agents adjusted to the limestone meal and flux used.

Further possibilities of making special lime are offered by the production of high-basic sinter on the sinter-strand where special attention has to be paid to the sulphur problem, or by the application of a procedure similar to the clinker production in cement manufacture.

ADVANTAGES OF SPECIAL LIME

Experiments in a 6-ton converter have been carried out in order to compare the effectiveness of the special lime in steel production with the traditional smelting procedures, and in order to answer the question whether soft burnt lime does in fact represent the optimum. These experiments were conducted with soft burnt lime of 10 to 30 mm grading and pelletized special lime which contained, besides lime, very densely dis-
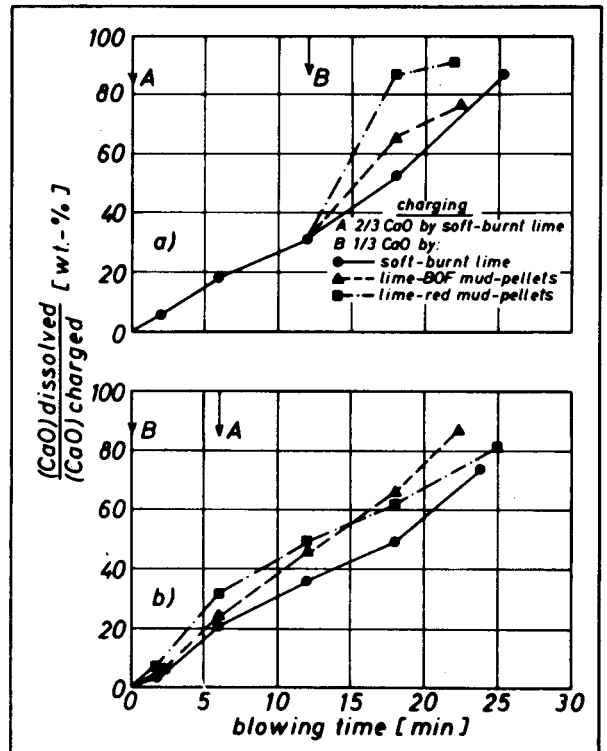

Fig. 9—Dissolution of lime in B.O.F.

tributed iron oxides, obtained from the exhaust gas in the basic oxygen plants, or else extracted from deposits (red slurry) resulting from alumina production from bauxite.
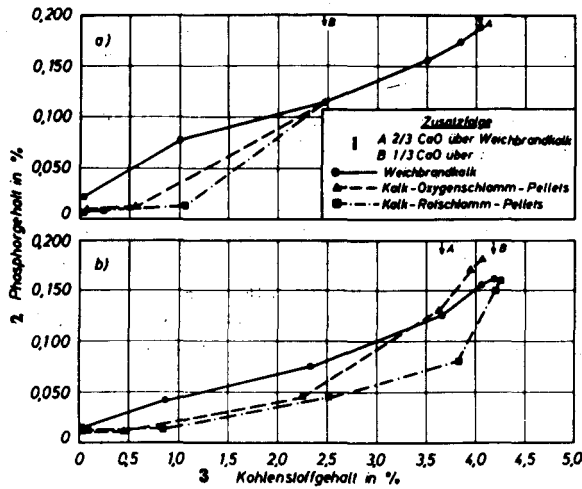

Fig. 10—De-phosphorisation by use of different lime products
1. **Flux mixture:**
   A. **2/3 CaO as soft burnt lime**
   B. **1/3 CaO as**
      ● **—Soft burnt lime**
      △ **—Lime BOF mut pellets**
      □ **—Lime—red slurry pellets**
2. **Phosphorus content.**
3. **Carbon content.**

It was found that by comparing the CaO quantities calculated from the slag analysis with the quantities of CaO fed (Fig. 9), the addition of special lime in comparison with the soft burnt lime clearly accelerated the lime dissolution. The early formation of a highly basic iron-rich slag is an important factor for good de-phosphorisation to which special attention has to be paid in Germany due to the composition of the pig-iron. In Fig. 10 we see the effect of special lime on the de-phosphorisation in comparison with the de-carburisation. The de-phosphorisation in all smelting processes of the first test series (Fig. 10a) is more or less constant until the different lime products are added. At a carbon content of 2,5 per cent we still find 0,11 per cent phosphorus in the bath. In comparison with procedures using only soft burnt lime the addition of special lime — containing oxide slurry — entails a considerably increased de-phosphorisation. This effect could still be augmented by the use of special lime with an addition of red oxide slurry.

The decomposition rate of the phosphorus is faster than the carbon decomposition rate when the special lime is added before the beginning of the blowing period (Fig. 10b). After a blowing period of 6 minutes at carbon contents of 3,6 to 3,9 per cent and at the same initial phosphorus contents, the phosphorus content, after adding the soft cement lime, still amounted to 0,125 per cent, whilst it was reduced to 0,080 per cent by the use of special lime with red slurry. This proved that a good mixture of lime and fluxes results in a fast slag formation.

The use of lime-fluorspar briquettes also accelerated the slag formation in a high-capacity converter, which was proved by acoustic measurements. The blowing period was extremely quiet even though the oxygen supply had been increased by 20 per cent and the blowing period reduced. During later tests the usual flux quantities could be reduced considerably. The oxygen supply could not be increased by more than 20 per cent thus excluding the possibility of further reduction of the injection period, as the de-gassing system was not adequate. This should be taken into consideration when designing new converters.

In another plant with converters of 250 ton capacity and a sufficiently large exhaust gas system, the oxygen supply could be increased from 500 Nm³/min to 1 100 Nm³/min for current operations, and up to 1 350 Nm³/min, i.e. over 5 Nm³/per ton per min for test purposes. Even more than 10 Nm³/per ton per min could be reached without difficulty in a pilot plant.

These results were obtained with fluxes containing iron oxides or alumina. Reference has already been made to the favourable effect of borate when we discussed a possible reduction of the fusion point of the dicalcium silicate. We find a similar application in the glass industry, e.g. with colemanite, we have available a natural mineral which contains calcium oxide and boron oxide. Due to an intense cracking process at temperatures exceeding approximately 200 °C, a very large surface is offered for dissolution in the slag. Colemanite begins to melt at 1 000 °C. If colemanite is used in the converter instead of fluorspar, in quantities that result in B_2O_3 contents of 0,5 to 1 per cent in the final slag, it causes a lowering of the melting point of the slag and a fast dissolution of the lime. The reactions between the very liquid slag and the metal bath are so fast that a special lance guide is needed to prevent the freezing of the slag. Better use can be made of the observed effects if colemanite is combined with a special lime which prevents the drying effect. If oxidation is sufficient, it is unlikely that the boron oxide will be reduced and the physical properties of the steel thereby affected. This has to be taken into consideration for the production of electric steel. The lowering of the melting point of the slag by the use of colemanite results in a better de-sulphurisation. Favourable results could be obtained by injecting high phosphorus pig iron, as the fluorspar could not be used due to the undesired reduction of the citric acid solubility of the phosphate slag caused by fluoride apatites.

Generally, it can be said that the use of special lime will find an increased interest in the Federal Republic of Germany, not only in the oxygen injection processes but also in electric steel production.

The research which we started a couple of years ago in this field for the oxygen injection process has also found great interest abroad. As far as we know, large industrial plants have been built in Japan and Australia for the production of special lime. The advantages of using special lime have been sufficiently proved by experiments.

The improvement of metallurgical reactions in the form of low phosphorus and sulphur contents, with the simultaneous concentration of the scattering ranges,

permits closer control of the smelting process. Due to the early slag formation, the injection process remains quiet and could be automated because of easy control.

The blowing period can be reduced by using an increased oxygen supply. By the use of special lime, the lance can mainly be concentrated on the de-carburisation instead of slag working. This is of great interest to foundries having pig iron of excellent quality which only needs to be de-carburised. In such cases, blowing periods of five minutes are no longer impossible unless a new limitation is presented by the scrap dissolution speed instead of the lime dissolution speed.

The increased output should compensate for the higher production cost of special lime compared with that of soft burnt lime. The possibility of an accurate control of the low phosphorus contents allows the production of steel with higher carbon contents by the interception procedure, and possibly the production of alloy steel in the converter.

Another advantage is the reduction of fluorspar fluxes, which may even be totally excluded by using special limes with appropriate composition. Fluorspar has not only become rare and expensive, but we have to expect that its use will one day be forbidden because of the environmental pollution caused.

It may be mentioned that with the use of special lime, residual slags should contain no free lime. This would offer a wide range of possibilities for the commercial exploitation of the slag, as the lime decomposition of the basic oxygen furnace slag restricted its use for road construction and other purposes. It can even be assumed that special lime with an adequate cementlike composition, would have cementlike properties or could be used for purposes never thought of hitherto.