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By-product-management in an integrated steel works on the example of steel-ladle-slag (SLS)

IModern steel production is related with a material input of almost twice the amount of the metallic yield. By-products of the steel making process are off-gas with a calorific content of one third of the primary energy purchased and slag with a total mass quantity of almost 32 % of the steel production. For the steelmaking industry, it is, therefore, an important challenge to find new applications and sellable products made of slag.
At Hüttenwerke Krupp Mannesmann, the blast-furnace (BF) slag is converted to blast furnace cement and then sold to the respective industry. Slags from both, BOF (LDS) and steel ladles (SLS) keep on being prepared and sold the traditional way. <war das gemeint?>
The following paper outlines some new ideas for innovative application of steel-ladle-slag.

The steelmaking site

Hüttenwerke Krupp Mannesmann GmbH (HKM) is an integrated steel works located in the South of Duisburg, a city on the river Rhein close to the German and Dutch border. The annual plant production capacity of almost 6.0 million t of continuously cast crude steel is especially designed for the demands of the customers, i.e. the rolling mills of Thyssen Krupp Stahl AG (TKS), Vallourec & Mannesmann Tubes S.A. (VMT) and Mannemannröhren Werke AG (MRW). The high-quality program offers a wide range of more than 2000 different steel grades for various applications.

The hot-metal production facilities comprise one coke oven battery, one sintering plant and two midsize blast furnaces. The steel plant can be divided in the hot metal ladle desulphurisation (with two independently operating treatment positions), two BOF-converters with a change vessel system, a secondary metallurgy configuration with two twin-tank vacuum degassers and three argon bubbling and refining stands. Three slab casters and two round billet casters serve for continuous casting, **fig. 1**. The three slab casters produce a wide range of steel grades in dimensions as requested by the customer and with natural edges. In the round billet casting department, grades for the production of seamless tubes as well as forging grades are cast in various diameters and cut to customers´ needs.

Utilising the add-on value. A wide range of raw materials is processed during steel making. The mineral components of the raw materials naturally result in several by-products representing add-ons to the desired amount of liquid steel. To make use of this additional value, processing of these by-products into common market products and on time shipment is an important target of the steel producing community all over the world. Acceptance of these products under environmental aspects as well as their approval as core business of the company are still weak points of this business.

Origin and amount of steel-ladle-slag (SLS)

At HKM, three different types of slag are generated. In addition to the BF-slag with an amount of approximately 1300 million t/a and the BOF-slag with an amount of approximately 0.400 million t/a, the raw steel-ladle-slag (SLS) with an amount of 0.150 million t/a is the quantity ranking third in the mass flow balance of the works´ by-products. This type of slag is formed by flux additions and chemical reactions in the secondary metallurgy devices of the steel making process and is used for:

- ♦ absorption of the deoxidation inclusions in liquid steel,
- ♦ absorption of alloy melting losses, BOF-slag carry over, ladle glaze and refractory erosion,
- ♦ steel desulphurisation work,
- ♦ recovery of the heat radiation from the melt during the waiting period *for* ***cast and casting*****. ???was bedeutet "for cast and casting", ?... until casting starts???**

The functions of the slag are, of course, related to the targets of the steel refining process [1; 2]:

- ♦ reducing the undesired steel accompanying elements (as, e.g. sulphur),
- ♦ improving the steel cleanliness requirements and
- ♦ adjusting the alloy contents and steel temperature.

The slag forming process starts with the beginning of tapping the converter. Slag forming agents and alloys are fed into the tapping stream to guarantee sufficient melt reaction in the ladle. The slag forming agents used at HKM cover burned lime, burned dolomite and, in some special cases of application, sand and fireclay. Both, the amount and sequence of the addition is related to the required steel analysis and downstream metallurgical process steps. Slag formation is completed by the absorption of the deoxidation products, the melt of ladle glaze, the erosion of refractory and the slag carry-over from the furnace. Due to the different treatment steps the slag composition changes during steel processing.

Finally, five major groups of SLS can be distinguished by composition depending on the steel type group. **Table 1** shows the average analysis and the portion of the slag type for the year-2003 production [3].

Treatment and separation of steel-ladle-slag, fig. 2. After casting, the residual liquid in the ladle comprises steel returns and metallurgical slag. The ladle is emptied into slag pots by using a crane. These containers are then railed to the slag pits, where they are poured in layers. After rapid cooling of the slag layers with spray water, the slag is dredged out of the pits by excavators. Heavy skulls of up to 20 t in weight are separated, divided into chargeable pieces by lancing [Brennschneiden? dann: flame cutting] and sent back to the converter scrap yard. The remaining slag is transported to a raw material storage and further processed in campaigns. All this separation work aims at recovering the steel skulls of less than 1 t per piece and the magnetic fraction below 6 mm particle size for recycling into the melting process.

The nonferrous SLS is approximately 0.100 million t/a and is divided into two fractions: 0 to 11 mm and 11 to 65 mm, the second fraction representing a 35-% fraction of the total amount.

Characteristics of steel-ladle-slag. Due to the requirements for a high desulphurisation potential and the necessity of refractory protection, the CaO- and MgO-contents of the liquid slag are kept within a certain range of deviation from the saturation index of CaO and MgO of the slag. Considering this deviation unavoidably occurring with technical processing in relation to chemical and thermal balances, the manufacturing strategy of today makes allowance for a booster dose as far as basicity is concerned. This strategy is used to avoid any acid input i.e. oxidising input from slag-carry-over from the BOF-furnace. This requirement for the core business results in negative characteristics for the by-product business: during down cooling of SLS, undissolved lime and magnesium-oxide additions in the slag cause the formation of free CaO and free MgO.

Generally, these fractions exhibit either granular or sponge like character [4]. Undissolved lime may be excluded during solidification, as shown in **fig. 3** [5]. Another reason for the occurrence of free lime is the transformation of tri-calcium-silicate (C_3S) to di-calcium-silicate (C_2S) at a temperature level of 1250 °C. These fractions caused by phase modification appear as streaks or films [6].

Looking at the mineral composition of SLS, beneath the typical main component mayenit ($C_{12}Al_{14}O_{33}$), other fractions like periclas (free MgO) and di-calcium-silicate (C_2S) are found in the SLS-mass. Based on X-ray-examinations it has been found that slag dissolution is basically caused by the crystalline transformation of di-calcium-silicate from α- to β- to γ-modification. The phase modification from β-C_2S to γ-C_2S below a transformation temperature of 500 °C is regarded most critical as far as destruction is concerned, because this modification is accompanied by an increase in volume of approximately 12 % showing the well-known effect of grain size destruction, not wanted by producers and users of slag-by-products [4; 7].

Undissolved lime and magnesia can also lead to destabilisation of SLS. Both mineral components are strongly influenced by volume increase during water absorption, an effect resulting in the complete discreation of the crystalline structure of the slag [8].

Application of steel-ladle-slag (SLS)

Recycling of SLS as a flux-substitute in the BF. Due to its tendency to disintegrate, a general utilisation of SLS in street construction is out of the question. As a consequence, SLS has, so far, mostly been supplied to the building industry to be used in lane construction or as filler material, applications to be regarded under their economic potential.

Reflecting its chemical composition, components CaO and Al_2O_3 make SLS a potential flux substitute in the BF. These ingredients open up the possibility of substituting dolomite and bauxite thus saving natural resources. Recycling of SLS reduces the number of participants in the complex mass flow in the BF by one fluxing agent. Simultaneously, this positively affects the logistics of blast-furnace burdening. Another advantage worth being mentioned is the reduced risk of achieving undesired material mixtures in the burdening areas [3].

The amount of SLS in the BF-burden depends on the desired basicity of the BF-slag. In case of a combination of self-fluxing sinter and pellets, the use of SLS would result in an undesired increase in the specific slag amount in the BF, since the correction of basicity by CaO input is related to an acidic addition of fluxes. In this case only the Al_2O_3-content of the SLS can be used as a substitute for natural bauxite additions to the BF-burden. In case of a more acidic iron ore basis, the CaO- and Al_2O_3-contents in the SLS will effectively substitute lime or limestone and bauxite additions in the BF-burden to control the BF-slag quality by adjusting the components [3]. It has to be mentioned that it is not useful to increase the Al_2O_3-content in the sinter to more than 1.0 %, because this would lead to a drastical increase in the low temperature disintegration tendency of the sinter.

Investigations pointed out that SLS will not be mechanically destroyed during conveyor transport to the BF. Thus, charging of SLS into the BF is neither expected to cause any pressure losses nor problems as regards gas permeability in the shaft. This also indicates that no abrasion of fines or early disintegration of SLS occurs compared to common BF-operation.

To come to a conclusion: SLS as processed in the fundamental and industrial trials at HKM can successfully be employed as a substitute for natural fluxes giving another opportunity to simplify BF-burden logistics by reducing the number of burden-ingredients [3].

Industrial scale tests with SLS as a flux-substitute in the BF. Since 2001, HKM is performing trials with SLS being processed and used in their blast furnaces on an industrial scale. In the beginning, SLS was screened to a grain size of 30/65 mm. To guarantee the required amount of correctives at a level of 20 kg/t hot metal, the grain size had to be changed to 11/65 mm. In the beginning of the campaign daily samples of the slag composition from the BF-storage were tested. In addition to the chemical composition the content of fines was determined. **Fig. 7** exemplarily shows the development of the CaO-content in the SLS over a period of 54 days. For comparison, the values for dolomite are included with the figure as well. For both agents the variation of CaO is matchable.

During testing, a few samples showed an increase in SLS-fines coming from the BF-storage. Several theories for the explanation of this effect have been set up:

- caused by the C_2S-disintegration in the slag pit, a high percentage of fines is transported to the preparation facilities. Since the SLS is sprayed with water to avoid or lower dust emissions during preparation, the fines stick to the surface of the coarse grain. This effect results in a lower screening efficiency of the installed preparation machines;

- another theory is based on the preparation of partially hot SLS. These portions disintegrate after preparation and screening due to C_2S-modification;
- the third theory for the generation of fines in the SLS-fraction 11/65 mm is the hydration of free burned lime in the mixture. Caused by the mechanical descaling of the slag pieces included, undissolved lime pieces are uncovered. The hydration reaction of burned lime is initiated by contact with humid air and for that reason, disintegration starts immediately.

To avoid all possible disintegration mechanisms, a short-time storage of the prepared SLS before consumption of the material is of importance. As an alternative, additional screening of the material just before burdening should be useful.

Use of SLS as fertilizer. Both the CaO-concentration and the small grain size make SLS a suitable fertilizer in agricultural application. Requirements for this utilisation is a sufficient solubility in the farmland ground with the target of neutralizing the acidic components in the ground to guarantee an increase in the pH-value of the ground. To meet these requirements, it has to be ensured that the content of residual metals in the fertilizer is harmless and below the environmental limits. Investigations on this subject came to the conclusion that SLS comprises very low contents of metals. This effect is originally caused by the metallurgical steel refining process, where metallic aluminium is used as a reducing agent for the metallic content of the ladle-slag. Due to this target the slag is low in residual metals and high in alumina.

In cooperation with the institute Kamperhof, which is the agricultural advisory board for *Thomas*-fertilizer, samples were taken on a regular basis and examined as regards their qualification as basic fertilizers. The tests include the measurement of the value adding components like CaO, MgO, and other basic substances and the reactivity, i.e. the reaction velocity of the slag.

As a result, **table 2** shows the chemical composition of the slag as an average of three different periods. In the case of SLS the summation of the CaO- and MgO-content is equivalent to a stoichiometric CaO-content of 53.2 %. Evaluation of this neutralisation factor in accordance with the method described in DIN EN 12945 resulted in a value of 59.2. It is obvious that SLS broadly exceeds the minimum of 40-% equivalent CaO-concentration required by the fertilizer-specification DüMV, even if the material exhibits a humidity of up to 14 %.

The dissolution of calcium and magnesium in light hydrochloric acid (reactivity test) lead to a result of 40 % compared to the minimum of 30 % demanded by the fertilizer-specification (DüMV). The reactivity of the magnesium-based substances reached the same level as the calcium-based substances, which can be interpreted as an excellent magnesium solubility. This further increases the efficiency of SLS as a fertilizer.

99.9 % of the SLS grain size is smaller than 3.15 mm and 50.4 % of the fines are below 0.315 mm, both figures satisfying the requirements for fertilizers.

The dissolution of SLS was tested on two samples representing different agriculturally used areas, one of them consisting of an acidic sand, the other of acidic clay. Several samples were analysed after a period of one week, one month and three months. The pH of the samples was determined in hydrochloric acid, as shown in **fig. 5**. The increase in yield due to fertilizing was tested by sowing yellow mustard (sort Litember) two days after conditioning of the ground. On both grounds, sand as well as clay an increase in yield was measured, **fig. 6**. The difference in effectiveness of SLS compared to common lime products was not significant. The quality of the HKM-SLS is characterised by its fast dissolution in the various types of ground, combined with a fast increase in the pH values.

With respect to this characteristics, SLS has proven an effective fertilizer to be used in agriculture and is expected to increase the plant yield noticeably [9].

Summary

Recycling of by-products is one of the major goals of the steel industry all over the world. A common practice is the reuse of iron containing materials as well as the utilisation of the calorific value of process gases. Nevertheless, recycling of other by-products can be extended to many other fields. The example of steel-ladle-slag (SLS) shows that, generally speaking, almost every by-product is of value in the primary steel making process. In the case of SLS, the metallic fraction can be used totally in the BOF. The only preparation work to be done is lancing [s.o.] the big skulls into chargeable pieces. In the BF, the SLS can be used to replace fluxing agents. The usable fraction ranges between 11 and 65 mm in grain size. With its typical composition of 44 % CaO, nearly 25 % Al_2O_3, and about 8 % of MgO, SLS replaces natural fluxing agents like dolomite and bauxite. This is more useful with an acidic than with a basic burdening of the BF. Investigations and industrial scale trials showed that SLS does not exhibit any obvious disadvantage compared to common burden materials.

Due to its chemical composition and its physical disintegration index, SLS in grain sizes between 0 to 3 mm can be effectively used as a fertilizer. The SLS is within the limits set by the fertilizer-specification and comparable to other steel plant products. Further development will include the SLS grain-size fraction between 3 and 11 mm. At present, this fraction is used in street and lane construction.

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Table 2: Chemical composition of the fertilizing slag averaged over three different periods [9]

	SLS	carbonatic limestone	converter lime
% CaO	44.0	46.5	42.6
% MgO	6.6	3.0	6.2
% CaO neutr. Value	59.2	52.4	50.6
% reactivity	40.4	72.4	45.9
% CaO reactivity	40.0	76.6	51.6
% MgO reactivity	41.4	26.0	17.9

Table 1: Classification of HKM´s steel-ladle-slag (SLS) [3]

grade		killed sulfur grade	sheet grade	IF-grade	roller bearing steel	controlled sulfur grade	SLS
fraction		49 %	30 %	15 %	3 %	3 %	100 %
CaO	%	45.0	41.0	42.0	41.0	20.0	44.0
Al_2O_3	%	24.0	29.0	27.0	11.0	36.0	24.9
SiO_2	%	7.0	5.5	4.0	21.0	21.0	9.1
MgO	%	8.0	10.0	8.0	5.0	5.0	7.9
MnO	%	0.10	0.16	0.07	0.34	4.44	0.25
S	%	0.95	0.54	0.38	0.26	0.09	0.70
FeO	%	0.60	1.00	0.80	1.21	1.50	0.80
Cr_2O_3	%	0.00	0.00	0.00	0.05	0.10	0.00
P_2O_5	%	0.02	0.02	0.02	0.02	0.02	0.02

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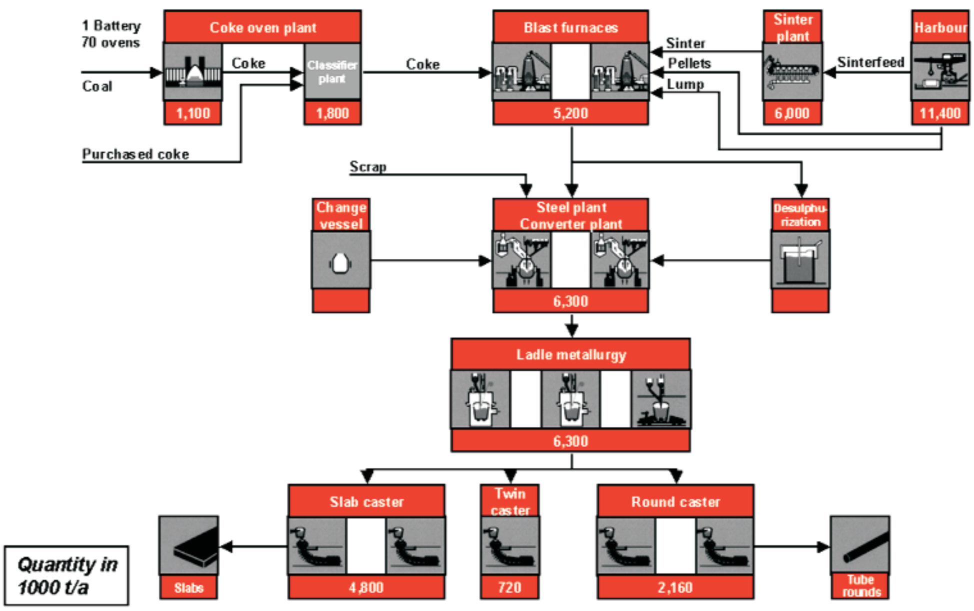

Fig. 1: Production facilities and material flow in HKM´s Duisburg-based steel plant

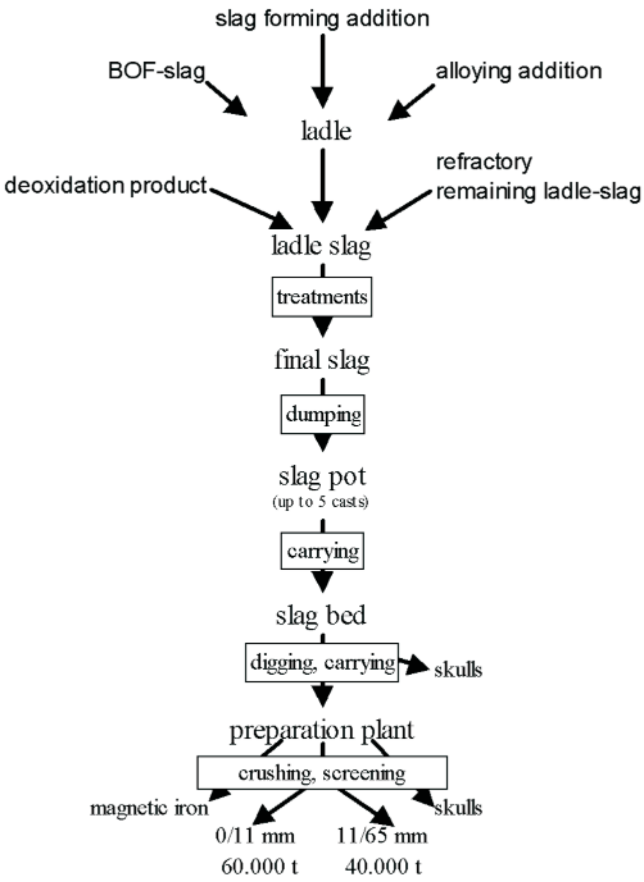

Fig. 2: Flow diagram of steel-ladle-slag (SLS)

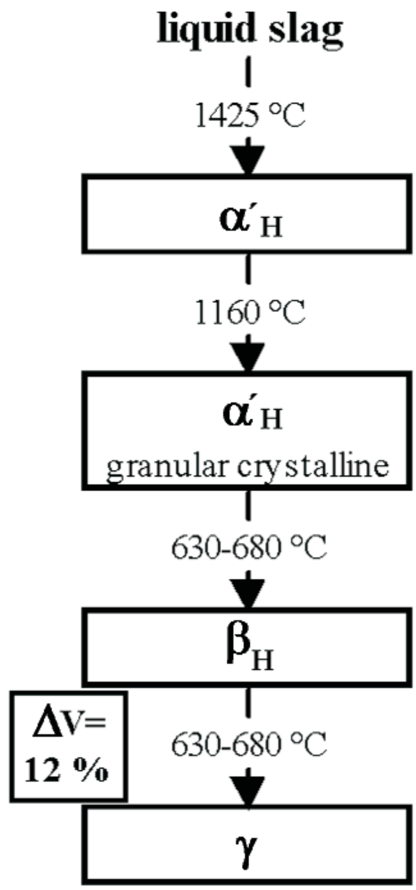

Fig. 4: Variation in C_2S modification during downcooling

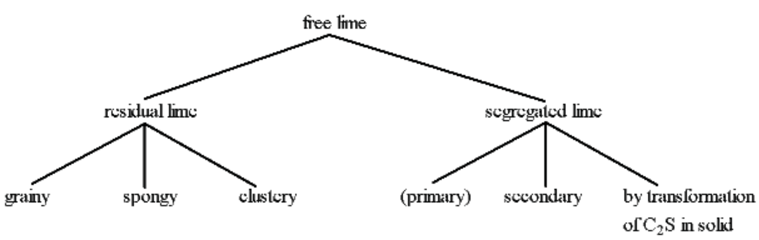

Fig. 3: Overview of free lime transformation [5]

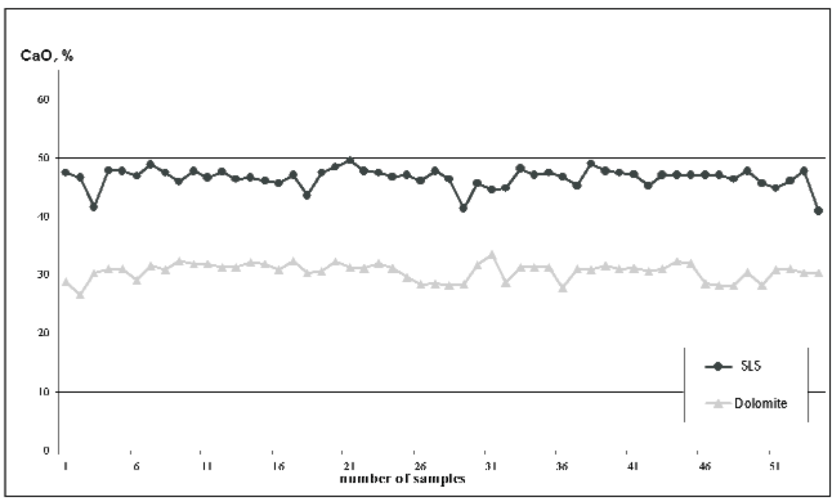

Fig. 5: Comparison of SLS and dolomite as regards compositional accuracy during blast-furnace burdening [3]

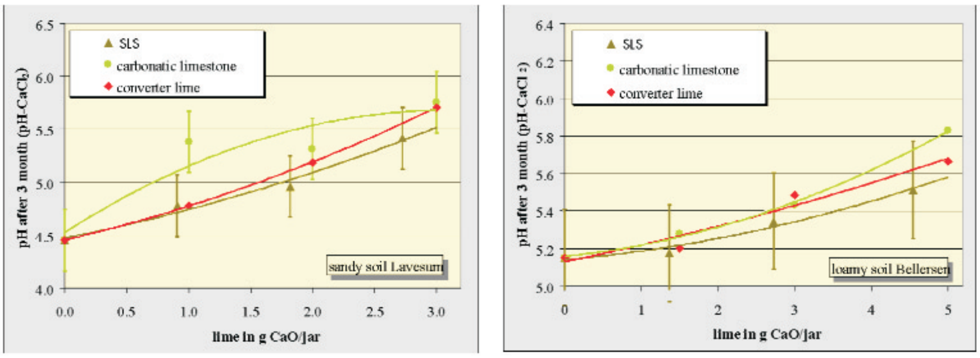

Fig. 6: pH-values of the grounds Lavesum and Bellersen, respectively, measured after a period of 3 months (corrected net weight???) [9]

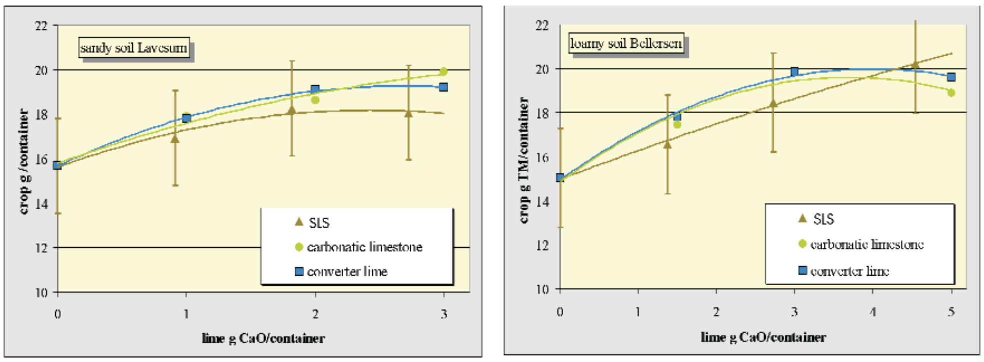

Fig. 7: Effect of yellow mostard sowed on sandy soil Lavesum and Bellersen [9]