

Synthesis and characterization of yellow gypsum from LD slag fines generated in a steel plant

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We describe here a simple method for synthesis of a value-added product (yellow gypsum) from Linz–Donawitz slag (LD slag), which is an industrial waste product of the steel industry. XRD analysis of the product confirmed the presence of anhydrite and gypsum phases as well as the presence of iron, silica and titanium in the form of fayalite and ilmenite phases. A weight loss of 17.26% was observed from the TG analysis, indicating the presence of mixture of the dihydrate, hemihydrate, soluble γ -anhydrite and insoluble β -anhydrite phases of gypsum in the product.

Keywords: LD slag, steel plant, synthesis and characterization, yellow gypsum.

It is estimated that the steel industry produces about 125 kg of steel slag per tonne of steel produced during the Linz–Donawitz (LD) process. This steel slag, known as LD slag, is rich in calcium-bearing silicates and some free lime along with metallic iron¹. This slag is processed in a waste recycling plant (WRP) so as to separate the magnetic iron portion and the non-magnetic portion by water quenching, solidification and using a series of magnetic separators. This is followed by crushing the slag to –300, –80 and –6 mm size fractions and then subjecting it to roll magnetic separation so as to recover the metallic iron. A typical chemical composition of the reject portion can be represented as 47–52% CaO, 2–13% free lime, 12–19% Fe, 1.5–2% P, 1.5–2% Al₂O₃ and 11–18% SiO₂ (refs 2, 3). Here iron is in the form of FeO and Fe₂O₃ as metallic iron is recovered in WRP.

As mentioned above, the reject non-magnetic portion is rich in different types of calcium silicate and therefore can be used in the iron sintering process as a good flux. However, due to its high phosphorus content (about 1.2–1.5%), this reject LD slag cannot be used in the sintering process because of the economic constraints involved in lowering the phosphorus content. It is therefore essential to explore other potential applications of this reject LD

slag. The reject portion (–6 mm size fraction) of the slag is mostly used as an aggregate in the construction of roads^{4–7}. This application is of economic significance due to the saving of natural resources such as gravel. Other applications include the use of LD slag as a starting material for production of cement clinker and as a fertilizer in the agricultural sector⁸. However, keeping in mind the enormous stockpile of LD slag, other applications need to be identified which can be helpful in the synthesis of value-added products of industrial importance.

In this context, the present work discusses the synthesis of yellow gypsum (calcium sulphate) from –60 mesh size LD slag fines. It is well known that gypsum has a wide range of applications, which include its use as a set retarder in the cement industry and as a starting material for production of different preformed building elements and plaster products in the medical field⁹. The use of gypsum as a soil conditioner for alkaline soils^{10,11} and in the production of Portland cement and sulphuric acid has been well documented^{12,13}. The significance of synthetic gypsum in the cement industry can be well understood by the fact that it can be an excellent replacement for natural gypsum and can therefore reduce the consumption of commercially mined gypsum. According to *Indian Minerals Yearbook 2012* (ref. 14), about 3.19 million tonnes of natural gypsum was produced in India during 2011–12. Therefore, synthetic gypsum produced from industrial waste such as LD slag can be useful in this scenario by effective conservation of natural gypsum. Also, recycling of gypsum produced as an industrial waste can be an alternative route for synthesis of sulphuric acid, which has a wide range of applications in the chemical industry. Thus, gypsum is an important value-added material having a wide range of applications. The aim of the present work was to therefore address the synthesis and characterization of a gypsum-type material synthesized from the –60 mesh LD slag fines at the Chemical Laboratory at Tata Steel Limited, Jamshedpur. The synthesized material was designated as ‘yellow gypsum’ owing to the yellow colour imparted by the presence of iron, as will be discussed in the subsequent sections in this article.

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Experimental

Materials and methods

The starting material for the experiment, viz. LD slag fines (–60 mesh) was obtained from the WRP at Tata Steel Plant Works, Jamshedpur. Sulphuric acid, AR-grade sucrose, hydrochloric acid and phenolphthalein indicator were obtained from E-Merck India. Borax and sodium carbonate were procured from M/s S.D. Fine Limited, India. All reagent solutions used for the experiments were prepared from double-distilled water.

Chemical composition of –60 mesh LD slag fines

The chemical composition of the –60 mesh LD slag fines was obtained by analysis of a solution acquired by fusing the sample with sodium carbonate and borax in a platinum crucible at 1000°C with the help of an appropriate muffle furnace. The fused melt was extracted with a dilute hydrochloric acid solution in water, which was then measured in an inductively coupled plasma spectrometer (ICP-make: Spectro, model: ARCOS equipped with CCD detector). The Leduc test was used to determine the free lime content¹⁵. The procedure described in ASTM D3872-05 (ref. 16) was followed in the determination of the FeO content. Loss on ignition (LOI) value was obtained at 1000°C by gravimetric analysis. LECO-make CS-200 instrument was used to analyse carbon and sulphur by combustion with non-dispersive infrared detection technique.

Experimental details for synthesis of yellow gypsum

A typical schematic depicting the synthesis procedure is given in Figure 1.

Ten grams of sample (–60 mesh LD slag) was weighed and transferred to a 250 ml glass beaker and was subjected to acid digestion by concentrated sulphuric acid (14 ml) along with 86 ml of double-distilled water at about $105 \pm 3^\circ\text{C}$ for 2 h with constant stirring. During digestion, all major impurities and other minor elements present in the sample get leached into the solution and calcium is precipitated as calcium sulphate. Silica is also precipitated in this process. The slurry thus formed is cooled and neutralized to pH 7.0 using 20% lime solution. The slurry is then filtered using Whatman filter paper no. 41 using a Buchner funnel and the solid residue is thoroughly washed with double-distilled water. The residue is then allowed to dry below 60°C for 24 h and is denoted as yellow gypsum. The chemical composition of the product is then determined by ICP and subjected to different characterization techniques. The filtered liquid (filtrate-1) being neutral in nature is disposed-off through an effluent treatment plant in a safe manner.

Chemical composition and characterization of yellow gypsum

Determination of sulphur trioxide content: The determination of sulphur trioxide (SO₃) content in materials similar to gypsum is useful in understanding the material compliance to the specifications of gypsum and similar products. The purity of the product is ascertained by the estimation of SO₃ content, which was determined by the method discussed in ASTM C471M–01 (ref. 17). This method is based on the assumption that the SO₃ content is attributed solely to the calcium sulphate content of the experimental sample, as it is devoid of significant amount of any other sulphate. According to this method, the sample is treated with barium chloride so as to precipitate barium sulphate which is then gravimetrically determined, followed by calculation of the sulphur trioxide equivalent of the sample.

Determination of impurities in synthetic gypsum: The fusion process described above was employed for sample preparation to determine the impurities in the synthesized yellow gypsum. The resultant sample solution was analysed by ICP. ASTM C471M–01 (ref. 17) was used to determine the silica content of the sample.

Characterization techniques: A laser particle size analyzer (make: Malvern Instruments Ltd, UK; model: Master sizer 2000E) was used for analysis of particle size of yellow gypsum. Mineralogical phase identification was done by X-ray diffraction (XRD) technique with the help of a PANalytical XRD Spectrometer (model XPERT-PRO) fitted with a Goniometer PW3050/60, with a minimum step size $2\theta: 0.001$. Copper was used as the anode and the generator settings were maintained at 30 mA and 40 kV respectively. A LECO-make thermogravimetric analyzer TGA-701 was used for the thermogravimetric analysis (TGA) of the synthesized yellow gypsum. The thermal analysis was carried out in three pyrolysis steps as described in Table 1.

The morphology of the material was confirmed with the help of scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) was used to obtain the chemical composition of yellow gypsum. A FEI 430 Nova-make Nano SEM was used for the SEM–EDS analysis. The SEM was equipped with a zirconia-coated tungsten filament along with EDS (make: Ametek) having a silicon drift detector (SSD). An accelerating voltage of 15 kV was maintained for all the measurements.

Results and discussion

Chemical composition of –60 mesh LD slag fines

Table 2 presents the chemical composition of the –60 mesh LD slag fines. It can be seen from the table that the

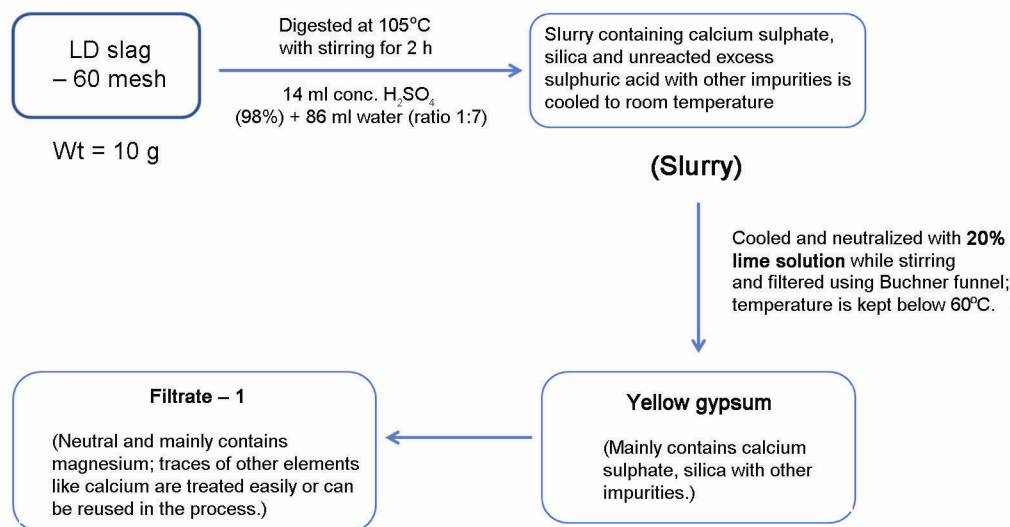


Figure 1. Process flow sheet of lab-scale production of yellow gypsum.

Table 1. Three stages of the pyrolysis of yellow gypsum

Pyrolysis					
Step-1		Step-2		Step-3	
Start temperature	108°C	Start temperature	450°C	Start temperature	550°C
End temperature – 1	450°C	End temperature – 2	550°C	End temperature – 3	900°C
Ramp rate	5°C/min	Ramp rate	3°C/min	Ramp rate	3°C/min
Ramp time	68 : 00 min	Ramp time	33 : 00 min	Ramp time	10 : 00 min
Hold time	0 min	Hold time	0 min	Hold time	15 min
Atmosphere	Nitrogen	Atmosphere	Nitrogen	Atmosphere	Nitrogen
Flow rate	8.5 l/min (medium high)	Flow rate	8.5 l/min (medium high)	Flow rate	8.5 l/min (medium high)
Complete time	End of step	Complete time	End of step	Complete time	End of step

Table 2. Chemical composition of Linz–Donawitz slag fines

Parameters	Values
% Fe ₂ O ₃	7.29
% FeO	11.61
% CaO	49.15
% SiO ₂	11.75
% P ₂ O ₅	2.32
% MgO	4.21
% MnO	0.397
% Al ₂ O ₃	1.00
% TiO ₂	0.934
% Cr ₂ O ₃	0.105
% LOI	11.02
Total (%)	99.8
% Free lime	11.9
% C	1.41
% S	0.19

composition is typical of LD slag as observed by other researchers^{2,3}. The material is rich in calcium, and iron is present in the oxide form. Table 2 represents the total chemical composition as the sum of all the components

(in oxide form), including iron. Also, iron is present in the form of FeO and Fe₂O₃; FeO was evaluated by following the procedure described in ASTM D3872-05 (ref. 16) and Fe₂O₃ content was determined by calculation. Thus, total iron in the sample can be expressed as the sum of the Fe₂O₃ and FeO iron components and therefore it can be concluded that iron is not present in metallic form in the sample, as mentioned in the introductory section.

Chemical composition of yellow gypsum

Determination of sulphur trioxide content: The SO₃ content was determined to be 40.45% and hence calcium sulphate in the sample was estimated to be 87.98%. This type of material can be therefore designated as type 2 and 3 gypsum respectively, according to the specifications mentioned in IS: 1290–1973 (ref. 18). Thus, it was ascertained that the synthesized material was a gypsum-type material. This concept has been substantiated by characterization of the material, which will be discussed below.

Table 3. Chemical composition of yellow gypsum

Parameters/sample	Unit	Fe ₂ O ₃	CaSO ₄	SiO ₂	P ₂ O ₅	MgO	MnO	Al ₂ O ₃	TiO ₂	Cr ₂ O ₃
Yellow gypsum	%	5.04	87.98	3.84	0.843	1.29	0.124	0.190	0.248	0.065

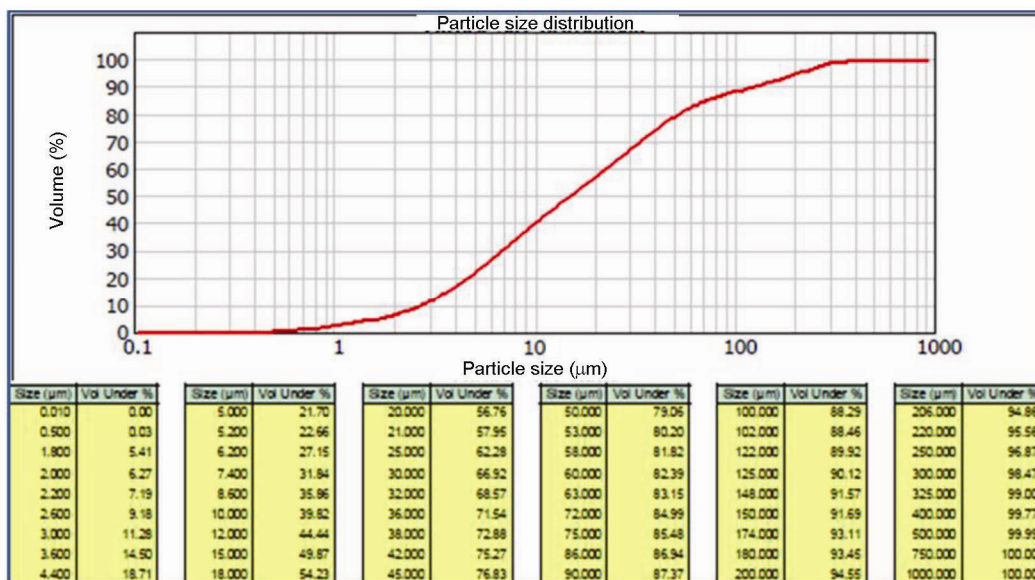


Figure 2. Particle size distribution plot of yellow gypsum.

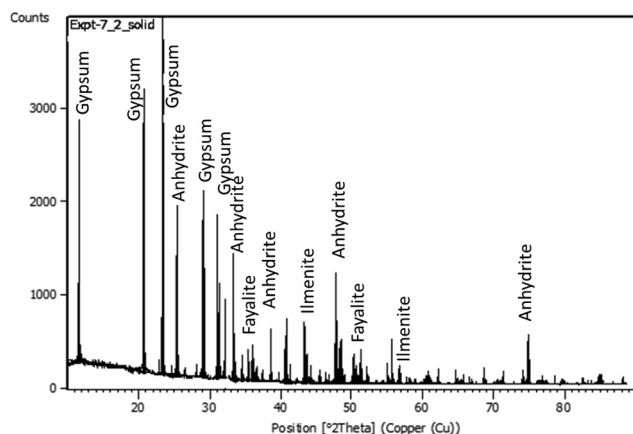


Figure 3. X-ray diffractogram of yellow gypsum.

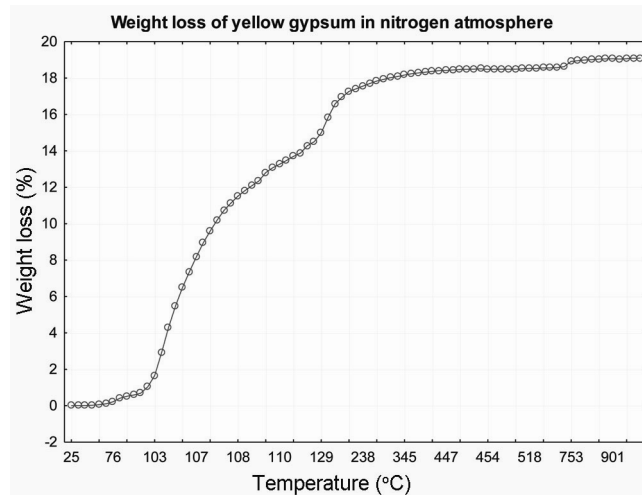


Figure 4. TG curve for yellow gypsum.

Analysis of impurities in the synthesized gypsum: The results of the analysis of impurities in the yellow gypsum sample are given in Table 3. It can be observed from Table 3 that the sample contains about 5% iron oxide, which is responsible for imparting the yellow colour to it, and therefore the sample is known as yellow gypsum. Also, silica is present to the tune of about 4%. The result obtained for silica by ICP analysis is similar to that obtained from the gravimetric procedure followed in ASTM C471M-01 (ref. 17).

Characterization of synthetic gypsum

Particle size analysis: Figure 2 plots the particle size distribution of the synthesized yellow gypsum. From the figure and the data, it can be concluded that the d₅₀ size of yellow gypsum is 15.081 µm. It can be observed that the particle size varies from 1.8 to 500 µm; the volume under 1.8 µm is 5.41% and that under 500 µm is 99.99%. Also, all particles are within 500 µm.

XRD analysis: Khan and Webster¹⁹ have discussed the qualitative identification of gypsum in solonchic soils by XRD technique, whereas Schultz²⁰ has discussed the semi-quantitative approach for bulk mineralogical analysis of the Pierre shale. Figure 3 presents the X-ray diffractogram of yellow gypsum. The main phases observed in the XRD analysis are anhydrite, gypsum, fayalite and illmenite. These findings correlate with the chemical composition of the synthesized yellow gypsum, which shows the presence of iron, silica and titanium in the sample as given in Table 3.

Thermogravimetric analysis: Eswaran and Zi-Tong²¹ have discussed the conversion of gypsum to anhydrite at about 200°C by thermogravimetric technique and have recommended the TGA method for determination of weight loss for samples containing high gypsum content. Basically, the weight loss of the gypsum sample is due to dehydration of the dihydrate gypsum to the anhydrous anhydrite form. Based on theoretical calculations, the water of hydration for gypsum phase ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is 20.91% and for the hemihydrate phase ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) it is 6.20%. The TG curve of yellow gypsum is represented in Figure 4, which indicates a weight loss of 17.26% at 200°C. This weight loss is less than the theoretical weight loss of the dihydrate gypsum and more than that of the hemihydrate phase. Hanna *et al.*²² have discussed the thermal behaviour of phosphogypsum. They observed that at around 151°C, the hemihydrate phase is formed and on further rise in temperature, i.e. at about 180–200°C, there is formation of the soluble anhydrite phase or the γ -anhydrite phase, as discussed by Deutsch *et al.*²³. The soluble anhydrite phase is metastable in nature and on further increase in temperature, gets completely dehydrated to form the insoluble β -anhydrite phase due to the liberation of residual water of the soluble anhydrite phase. Thus, it can be concluded that yellow gypsum consists of a mixture of the dihydrate,

hemihydrate, soluble γ -anhydrite and insoluble β -anhydrite phases of gypsum. These findings correlate with the X-ray analysis which identifies the dihydrate and anhydrite phases.

SEM analysis: The morphology of the yellow gypsum sample can be observed from the SEM photomicrograph given in Figure 5. It can be observed that gypsum is present as tubular and radiating elongated crystals as discussed by Ausset *et al.*²⁴, thus confirming the typical morphology of gypsum crystals.

Figure 6 represents the point-wise analysis of a representative area of the sample under 10,000 \times magnification. From this figure and elemental analysis data in Table 4, it can be confirmed that the sample contains high calcium and sulphur content. The elemental analysis of this area of the sample can be further understood as follows:

Points 3, 6 and 9 are rich in silica and are present as dispersed clusters among the gypsum crystals represented by the other points which are rich in calcium, sulphur and oxygen.

Conclusion

Yellow gypsum was synthesized by acid leaching of –60 mesh LD slag fines. The product was subjected to characterization using different techniques, namely XRD, TGA and SEM–EDS. XRD analysis revealed the presence of gypsum and anhydrite phase which could be correlated with the findings from TGA. Also, TGA suggested that the sample consists of a mixture of dihydrate, hemihydrate, soluble γ -anhydrite and insoluble β -anhydrite phases of gypsum. SEM–EDS analysis also supported these findings by confirming the presence of calcium, sulphur, oxygen and silica in the sample. The synthesized yellow gypsum can be of great value in the Portland cement industry as it can serve as an excellent replacement

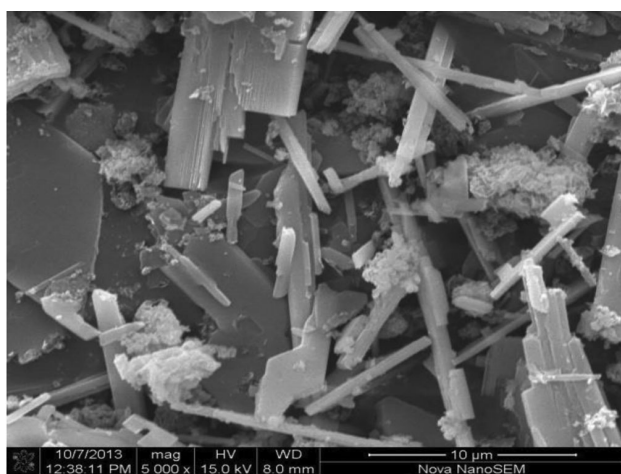


Figure 5. SEM photomicrograph of yellow gypsum.

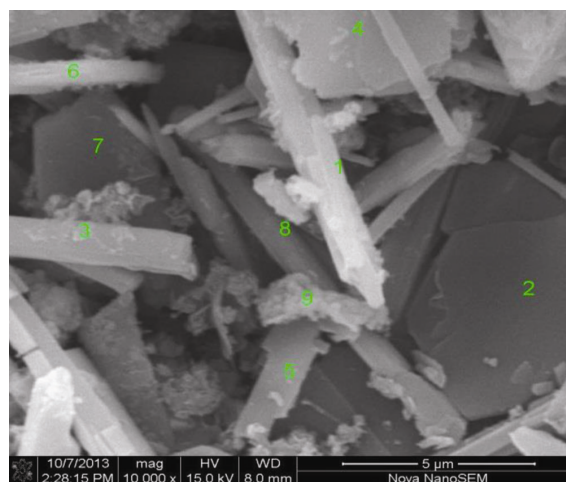


Figure 6. SEM photomicrograph examined for EDS analysis at 10,000 \times magnification.

Table 4. SEM–EDS analysis for a representative area of yellow gypsum

Point no.*	% O	% Mg	% Al	% Si	%P	%S	%Ca	%Ti
1	33.37	0.52	0.33	1.93	2.39	25.43	35.45	0.58
2	31.50	0.22	0.71	0.97	1.32	27.39	37.38	0.51
3	13.96	0.93	0.61	2.63	2.35	29.74	48.61	1.16
4	15.37	0.00	0.50	1.14	2.03	32.80	47.79	0.38
5	14.14	0.89	1.24	2.20	1.97	30.92	47.42	1.22
6	10.61	0.31	0.60	2.06	2.78	29.31	52.04	2.28
7	5.25	0.17	0.46	1.34	1.77	30.88	57.90	2.23
8	29.23	0.42	0.46	2.54	2.18	26.36	38.21	0.60
9	19.33	0.98	1.00	3.85	3.36	29.08	41.04	1.37

*Point numbers as given in Figure 6.

for natural gypsum. Therefore, the present work can be envisaged as an appropriate step in the conservation of natural gypsum, and extensive mining of the same can be reduced and controlled. Also, recycling of gypsum produced as an industrial waste can be an alternative route for synthesis of sulphuric acid, which has a wide range of applications in the chemical industry. Thus, gypsum is an important value-added material having a wide range of applications and has immense economic value. The present work has therefore achieved its major objective by presenting a route for the synthesis of a value-added product (gypsum) from LD slag, which is an industrial waste product of the steel industry. An Indian patent application bearing application number 572/KOL/2014 has also been filed on 23 May 2014 on the basis of this study.

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