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1 **Characterization of Gypsum Synthesized from LD Slag fines generated at Waste**
2 **Recycling Plant of a Steel Plant**

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9 **Abstract:**

10 The present work is devoted to the characterization of gypsum synthesized in
11 laboratory scale by the atmospheric leaching of -60 mesh LD slag fines generated from Waste
12 Recycling Plant (WRP) during the Linz-Donawitz process of steel making at Tata Steel plant,
13 Jamshedpur, India. The main objective of the present work was to synthesize and characterize
14 gypsum which is a value added product from LD slag which is a waste product of the steel
15 industry. The techniques used for the characterization were X-ray diffraction (XRD),
16 scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) and
17 thermogravimetry (TG) techniques. The XRD analysis revealed the presence of the anhydrite
18 and gypsum phases in the product material as well as the presence of silica in the form of
19 coesite. This observation was further correlated by the TG analysis which indicated that the
20 synthetic gypsum was a mixture of gypsum (dihydrate), hemihydrate, soluble γ -anhydrite and
21 insoluble β -anhydrite phases of gypsum. The morphology of the material was found to be like
22 tabular crystals alongwith the presence of intermittent needle-like and rod like structures as
23 observed from the SEM micrographs. The chemical composition was further confirmed by
24 SEM-EDS analysis. The purity of the product was also estimated to be 86.12% calcium

1 sulphate by estimation of sulphur trioxide content. These findings have been discussed in
2 detail in the subsequent sections of the paper.

3 **Key words:** gypsum, LD slag, leaching, characterization, anhydrite, hemihydrate, calcium
4 sulphate

5 **1.0 Introduction:**

6 Steel slag is produced during the Linz-Donawitz process or the LD process in an
7 integrated steel plant at a rate of about 125 kg/ton of steel. This steel slag, also known as LD
8 slag is highly basic in nature as it is rich in calcium bearing mineral phases like mono, di and
9 tri calcium silicates alongwith free lime and some metallic iron¹. This metallic iron is
10 recovered in a waste recycling plant (WRP) through a series of sequential steps such as water
11 quenching, solidification and by using a series of magnetic separators. The non-magnetic
12 fraction which is -6mm in size is stocked and is generally used as an aggregate for road
13 construction²⁻⁵. Chemically this reject has a typical composition of about 47-52% CaO, 2-
14 13% free lime, 12-19% Fe, 1.5-2% P, 1.5-2% Al₂O₃ and about 11-18% SiO₂⁶⁻⁷. Here, iron is
15 in the form of FeO and Fe₂O₃ as metallic iron was recovered in the waste recycling plant
16 (WRP).

17 Apart from being used for road construction, steel slag has other important
18 applications which are described further. Steel slag can be used as a sinter ore fluxing agent
19 where it can serve as an excellent replacement for commercial lime. Addition of slag can
20 enhance the quality and also reduce the fuel consumption owing to the liberation of heat in
21 the Fe and FeO oxidation reaction, thus reducing the cost of sinter ore⁸. However, this
22 application has it's own share of limitations as the steel slag reject contains about 1.2-1.5%
23 phosphorus, which is not acceptable due to additional costs involved in removal of
24 phosphorus. Other uses for steel slag can be in the form of raw material for cement clinker,
25 as a fertilizer for acidic soils and in cement and concrete production⁹. Steel slag has also been

1 explored as material for carbonation in the area of carbon dioxide sequestration¹⁰. These
2 various applications indicate that steel slag cannot be simply considered as a waste material
3 of the steel making industry. However, at the same time these applications alone cannot take
4 care of the huge stockpile of this slag at the enormous rate at which it is produced. Therefore,
5 it is necessary to find other economical and novel ways to manufacture or produce more
6 materials of industrial importance from LD Slag fines. In other words, value addition of steel
7 slag needs to be explored so as to produce materials having diverse applications in the
8 chemical industry and other related sectors.

9 In this context, the present work discusses the synthesis of synthetic gypsum (calcium
10 sulphate) by the atmospheric leaching of LD Slag with dilute sulphuric acid at about 100 °C.
11 It was observed that by following this process, calcium sulphate of purity more than 86%
12 could be synthesized. Gypsum is greatly used in the ammonium sulphate and the pottery
13 industry. Synthesis of gypsum can also highly impact the cement industry by a significant
14 reduction in the use of commercially mined gypsum used in the manufacture of Portland
15 cement¹¹. It is also useful as a raw material for producing plaster products and other
16 preformed building elements such as wall boards¹¹. It is also utilized in the agriculture sector
17 as a fertilizer¹²⁻¹³. Thus, the significance of gypsum can be very well understood from these
18 different applications. The present study aims to explore the possibility of synthesis and
19 characterization of a value added product, gypsum from LD slag, which is a waste product of
20 the steel industry by a simple chemical process. An Indian patent application bearing
21 application number 744/KOL/2014 has also been filed on the basis of this study, which
22 expresses the novelty of the present work.

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1 2.0 Experimental:

2 2.1 Materials and methods:

3 LD slag fines of different sizes (0-6mm) were obtained from the Tata Steel Plant
4 Works at Jamshedpur. The synthetic gypsum has been synthesized from the -60mesh fines.
5 AR grade sucrose, hydrochloric acid, sulphuric acid and phenolphthalein indicator were
6 procured from E-Merck India respectively. Sodium carbonate and borax were obtained from
7 M/s. S.D.Fine Limited, India. Double distilled water was used in the preparation of the
8 different reagent solutions.

9 2.2 Chemical composition of -60 mesh LD slag fines:

10 The LD slag fines (starting material for the synthesis) were analyzed for the chemical
11 content by a fusion process, using sodium carbonate and borax (2:1 ratio) at 1000 °C in a
12 platinum crucible in a suitable muffle furnace. The fused melt was extracted with 20%
13 hydrochloric acid in water and the obtained solution was then analyzed in an Inductively
14 Coupled Plasma spectrometer (ICP – make: Spectro, Model: ARCOS equipped with CCD
15 detector). Free lime content was analyzed by using the Leduc test¹⁴. This test involves
16 dissolution of free lime from ground slag using a 10% sugar solution and titration with a 0.1
17 N sulphuric acid (H₂SO₄) solution after filtration. Phenolphthalein was used as the indicator.
18 The FeO content was determined as per the procedure described in ASTM D3872-05¹⁵. Loss
19 on ignition (LOI) was determined at 1000 °C by gravimetric analysis in a muffle furnace.
20 Carbon and Sulphur were analyzed by combustion and infrared cell detection method using
21 the LECO make CS-200 instrument.

22 2.3 Experimental details for synthesis of synthetic gypsum:

23 10 g of LD Slag sample (-60 mesh) is taken in a glass beaker and digested using 14ml
24 of concentrated sulphuric acid (98%) mixed with 86ml of water at about 105 ± 3 °C for two
25 hours with stirring. During the process of digestion all the major impurities in the LD Slag

1 viz., Fe, MgO, Al₂O₃, TiO₂, P₂O₅ and other minor elements like Cr₂O₃, V₂O₅, etc., get
2 leached into the solution and calcium is converted into calcium sulphate which is insoluble.
3 Along with the calcium sulphate, silica also remains insoluble. The slurry thus formed is
4 cooled and filtered under suction using the Whatman Filter paper No 41 and washed with
5 water. The solid obtained is dried below 60 °C for 24 hrs and designated as residue 1.

6 The product thus formed was then analyzed for its chemical composition and
7 characterized by different techniques as described in the subsequent sections. The filtered
8 liquid (filtrate – 1) was further neutralized with the help of ammonia to recover iron,
9 titanium, aluminium and phosphorus as their sulphates and was designated as residue 2. This
10 solid formed from the leachate contains around 40% iron along with titanium and
11 phosphorus. The filtrate obtained in this process (filtrate -2) was observed to be neutral and
12 found to contain traces of magnesium and could be easily disposed off through an effluent
13 treatment plant.

14 **2.4 Chemical composition and characterization of synthetic gypsum:**

15 **2.4.1 Determination of sulphur trioxide content:**

16 The significance of determination of the sulphur trioxide (SO₃) content in gypsum like
17 materials is to determine the compliance of the material to the specifications of gypsum and
18 similar products. The estimation of SO₃ content provides a way to ascertain the purity of the
19 synthesized gypsum. Therefore, SO₃ content of the synthetic gypsum was determined by
20 following the procedure described ASTM C471M – 01¹⁶. As per this method, the calcium
21 sulphate content can be determined from the SO₃ content of the sample on the basis of the
22 assumption that the experimental sample contains an insignificant amount of sulphate other
23 than calcium sulphate and therefore the SO₃ content is attributed to the amount of calcium
24 sulphate present in the sample. In this test method, sulphate is precipitated from an acid
25 solution of the gypsum with barium chloride (BaCl₂). The precipitate is filtered and weighed

1 as barium sulfate (BaSO_4) and sulfur trioxide (SO_3) equivalent is calculated. Thus,
2 determination of sulphur trioxide content in the experimental sample provides a way for
3 estimating the calcium sulphate content of the sample.

4 **2.4.2 Determination of impurities in synthetic gypsum:**

5 The impurities in the synthetic gypsum synthesized in the laboratory were determined
6 by a similar fusion process as described in section 2.2 and analyzed by the ICP. The silica
7 content was also determined by the procedure described in ASTM C471M – 01¹⁶ so as to
8 compare the values obtained from ICP for the same. As per this method, silica is determined
9 by the weight difference of the experimental sample after dissolving the same in dilute
10 hydrochloric acid.

11 **2.4.3 Characterization techniques:**

12 The particle size analysis of the synthetic gypsum was carried out by using a Laser
13 Particle Size analyzer (make: Malvern Instruments Ltd., UK; Model: Master sizer 2000E).
14 X-ray diffraction (XRD) was used for the phase identification analysis for the sample and
15 was performed by using a PAN Analytical XRD Spectrometer Model XPERT-PRO fitted
16 with a Goniometer PW3050/60 with a minimum step size 2θ : 0.001. The anode material was
17 copper and the generator settings were maintained at 30mA, 40kV respectively.

18 Thermogravimetric analysis (TGA) was carried out by a thermogravimetric analyzer, TGA-
19 701 (make: LECO, Corporation, USA). TGA was used for study of the weight loss of the
20 synthetic gypsum sample synthesized in the laboratory. The sample was heated from room
21 temperature to 107 °C and further in three steps to 900 °C in nitrogen atmosphere. Scanning
22 electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) was used for
23 further confirmation of the phases in the synthesized gypsum and to get an overview of the
24 chemical composition of the synthesized material. The SEM-EDS analysis was performed by
25 using a FEI 430 Nova make Nano SEM equipped with a tungsten filament coated with

1 zirconium oxide and coupled with a Ametek make energy dispersive spectrometer (EDS)
2 using a silicon drift detector (SSD). The acceleration tension was kept at 15 kV for all the
3 measurements.

4 **3.0 Results & discussion:**

5 **3.1 Chemical composition of -60 mesh LD slag fines:**

6 The chemical composition of the starting material i.e. the -60 mesh LD slag fines has
7 been presented in table 1. It can be observed that the fines are rich in calcium and also
8 contain iron in the oxide form. Silica is also a major part of the chemistry of these fines. This
9 is a typical composition of LD slag as observed by other researchers⁶⁻⁷.

10 **Table 1:** Chemical composition of LD Slag fines

11 Parameters	11 Values
12 % Fe₂O₃	7.29
13 % FeO	11.61
14 % CaO	49.15
15 % SiO₂	11.75
16 % P₂O₅	2.32
17 % MgO	4.21
18 % MnO	0.397
19 % Al₂O₃	1.00
20 % TiO₂	0.934
21 % Cr₂O₃	0.105
22 % LOI	11.02
23 Total (%)	99.8
24 % Free lime	11.9
% C	1.41
% S	0.19

1 The total chemical composition given in table 1 is the sum of all the oxide components
2 including iron. Iron is present in the form of % FeO and % Fe₂O₃ out of which % FeO was
3 determined by procedure described in ASTM D3872-05¹⁵ and Fe₂O₃ content was determined
4 by calculation. Total iron in the sample is therefore the sum total of the iron of the Fe₂O₃ and
5 FeO components and therefore iron is not present in metallic form in the sample as
6 mentioned in the introductory section. Also, % free lime is a part of the % CaO content
7 determined by ICP. This free lime content was determined by the Leduc test¹⁴ and is
8 expressed as CaO equivalent % (CaO + Ca(OH)₂). During ICP analysis, the entire portion of
9 calcium is represented as % CaO as shown in above Table 1.

10 **3.2 Chemical composition of synthetic gypsum:**

11 **3.2.1 Determination of sulphur trioxide content:**

12 As discussed in section 2.4.1, sulphur trioxide content of the experimental sample was
13 determined by following the procedure described in ASTM C471M – 01¹⁶. The SO₃ content
14 was found to be 47.44% and therefore the calcium sulphate content was estimated as 86.12%.
15 As per the specifications made for gypsum mineral in IS: 1290-1973¹⁷, a material of this
16 nature is typically denoted as Type 2 and 3 gypsum respectively. Thus, the purity of the
17 synthesized gypsum was determined and it was also ascertained that the material was
18 gypsum. This has been further substantiated by XRD analysis, SEM-EDS analysis and TGA
19 study of the synthesized material.

20 **3.2.2 Analysis of impurities in the synthesized gypsum:**

21 Impurities in the synthetic gypsum were determined by using ICP Spectrometer by the
22 fusion process discussed in section 2.2. The results of the analysis (carried out in duplicate)
23 have been presented in table 2, wherein it can be observed that the SiO₂ was 12.52 %, Fe₂O₃
24 was 0.24 % and rest of the impurities were less than 0.10%. In addition to the analysis of the
25 impurities by ICP spectrometer, SiO₂ analysis was confirmed by following the procedure

1 prescribed in ASTM C471M – 01¹⁶. The complete chemical composition of the synthetic
 2 gypsum can be observed from table 2. The major components are calcium sulphate and silica
 3 which are 86.12% and 12.52% respectively.

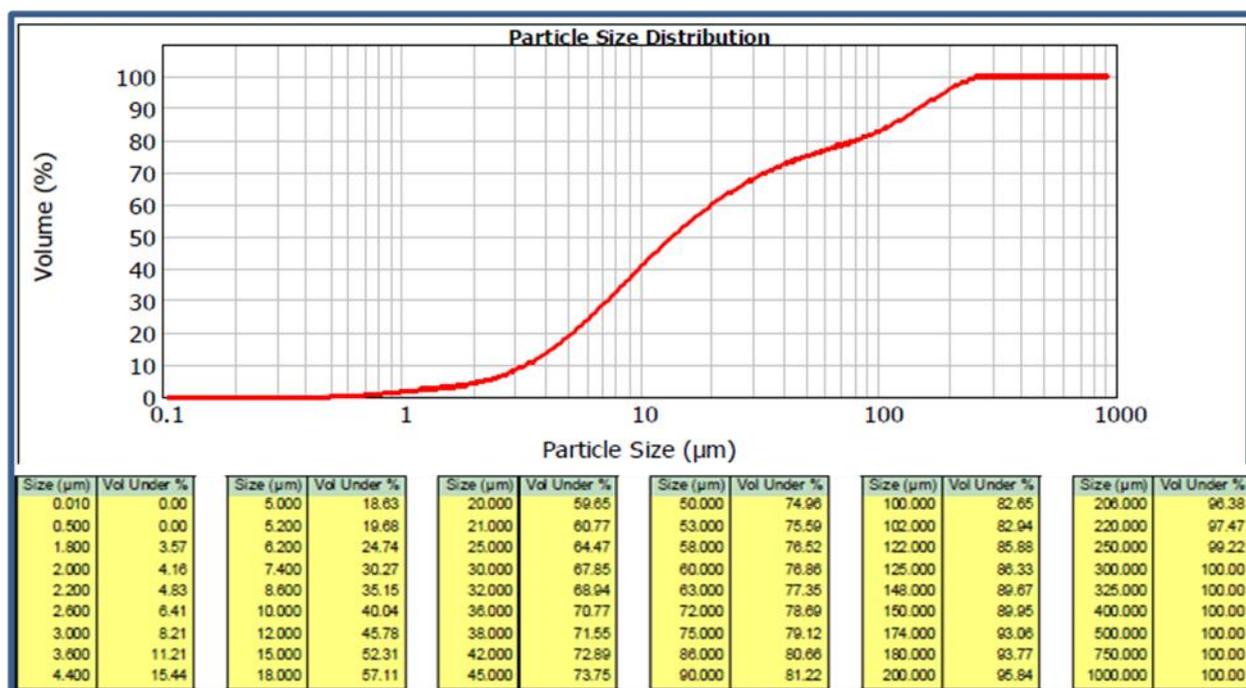
4 **Table 2:** Chemical composition of synthetic gypsum

Parameters / Sample	Unit	Fe ₂ O ₃	CaSO ₄	SiO ₂	P ₂ O ₅	MgO	Al ₂ O ₃	TiO ₂	Cr ₂ O ₃
Gypsum	%	0.240	86.12	12.52	0.030	0.068	0.057	0.022	0.020

6 3.3 Characterization of synthetic gypsum:

7 3.3.1 Particle size analysis:

8 Figure 1 depicts the complete picture of the particle size analysis and it was observed
 9 that the particle size varies from 1.8µm to 250 µm and volume under 1.8 µm is 3.57% and
 10 volume under 250 µm is 99.22%. Thus, it can be inferred that all particles are within 250 µm.



11 **Figure 1:** Volume under % at different particle size for synthesized gypsum

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3.3.2 XRD Analysis:

The synthetic gypsum was qualitatively identified by X-ray diffraction technique as discussed by Khan and Webster¹⁸. The major phases observed in the XRD pattern (figure 2) were anhydrite and gypsum. The presence of silica was confirmed by the identification of coesite phase. These findings confirm the identity of the synthetic gypsum and also correlate with the chemical analysis of the material.

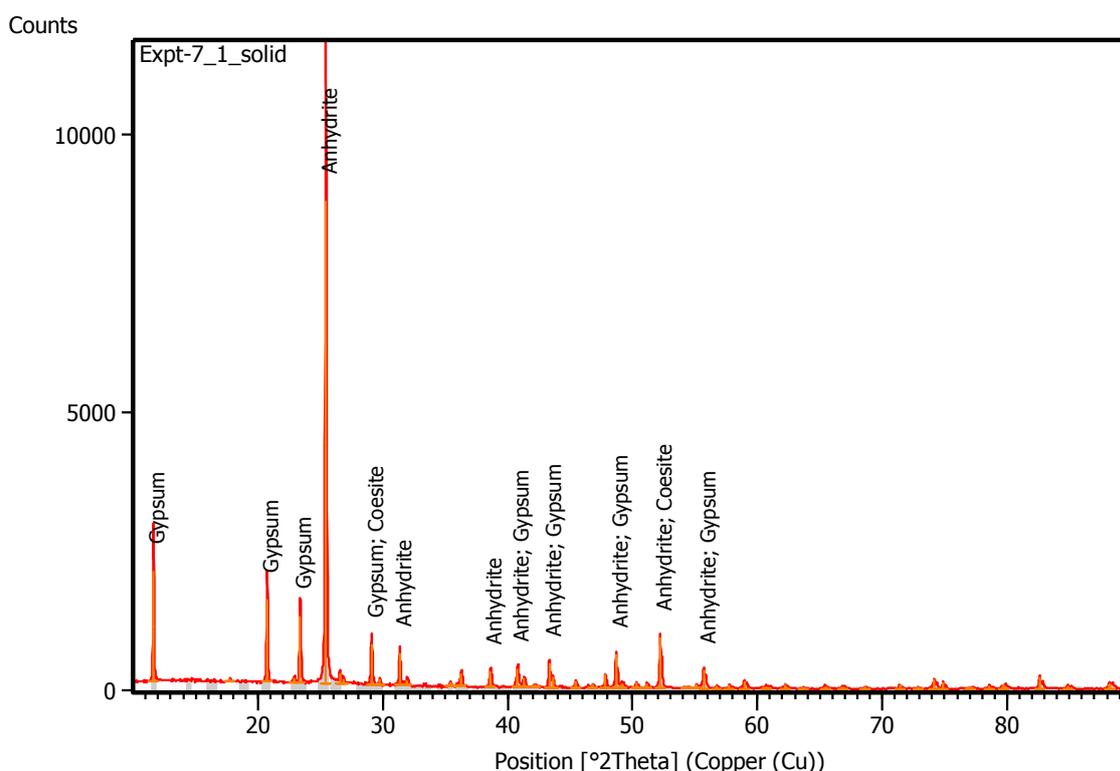


Figure 2: XRD pattern of synthetic gypsum synthesized in the laboratory.

Quantification of the different phases in the XRD pattern was not attempted as different researchers have expressed difficulty in phase quantification for gypsum. For instance, Eberl¹⁹ had observed that during grinding of the sample for analysis, loss of constitutional water occurs leading to anomalous results. A similar observation has been made by Roy et al.²⁰ wherein they reported that dehydration of the sample takes place during grinding, which

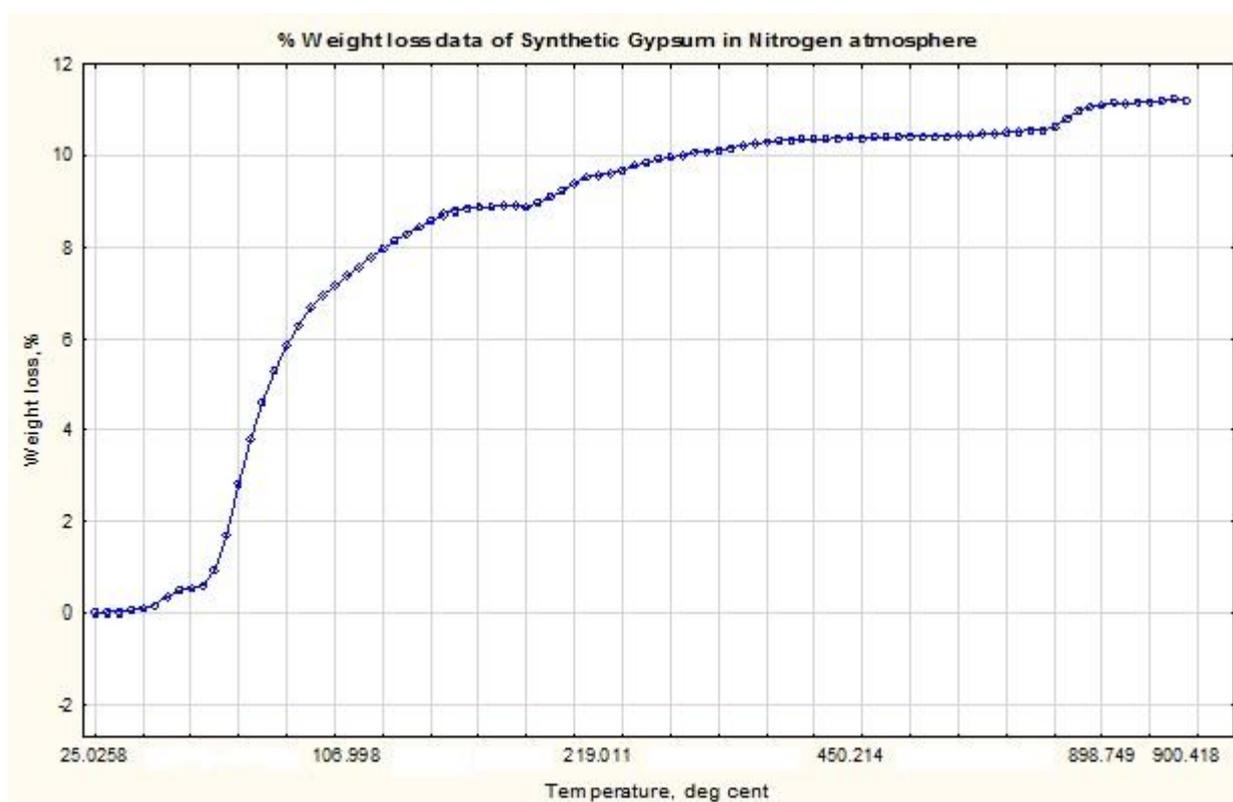
1 can lead to the formation of anhydrite phase dominantly over the hemihydrate phase and thus
2 misleading the overall results. Herrero et al.²¹ have also mentioned that the XRD approach of
3 phase quantification in gypsum can be very much confusing and described gypsum as a
4 “tricky material” in this context.

5 **3.3.3 Thermo Gravimetric analysis:**

6 Thermogravimetric analysis (TGA) study of gypsum has been discussed by Eswaran
7 and Zi-Tong²² during the study of the conversion of gypsum to anhydrite at about 200 °C by
8 thermogravimetric technique. Theoretically, gypsum phase ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) has 20.91% of
9 water of hydration and hemihydrate phase ($\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$) has 6.20% of water of hydration.
10 Figure 3 represents the thermogravimetric curve of the synthetic gypsum. It can be observed
11 from the figure that the gypsum produced in the laboratory had a weight loss of 9.36% at
12 200°C which is more than that of hemihydrate phase and less than that of gypsum when
13 compared to theoretical values. This observation can be understood by referring to the work
14 of Hanna and co-workers²³ wherein the thermal behavior of phosphogypsum has been
15 discussed. It was observed that at around 151 °C the hemihydrate phase was formed and on
16 increasing the temperature to about 180 -200 °C, the soluble anhydrite phase or the γ -
17 anhydrite phase is formed²⁴. This γ -anhydrite phase is metastable in nature and on further rise
18 in temperature, gets fully dehydrated and the insoluble β -anhydrite phase is formed with the
19 liberation of the residual water of the γ -anhydrite phase. It can be thus, inferred that the
20 synthetic gypsum is a mixture of gypsum (dihydrate), hemihydrate, soluble γ -anhydrite and
21 insoluble β -anhydrite phases of gypsum.

22 The findings from the TGA study can be correlated with the XRD analysis, which
23 identifies the gypsum and the anhydrite phases. However, the hemihydrate phase was not
24 identified in the XRD analysis. This observation can be explained on the basis of the study of
25 Murat²⁵ who reported the superposition of peaks of the gypsum and hemihydrate phases in

1 the x-ray diffraction pattern. Similarly, Roy et al.²⁰ have reported that during sample
2 preparation for XRD analysis of gypsum type samples, dehydration occurs during grinding,
3 which can lead to the formation of anhydrite phase dominantly over the hemihydrate phase.
4 Thus, it will be difficult to identify the hemihydrate or bassanite phase in the gypsum sample
5 by XRD analysis alone and therefore TGA can provide the supporting information leading to
6 our earlier observation that synthetic gypsum is a mixture of gypsum (dihydrate),
7 hemihydrate, soluble γ -anhydrite and insoluble β -anhydrite phases of gypsum. This
8 observation was also made earlier by Posnjak²⁶.

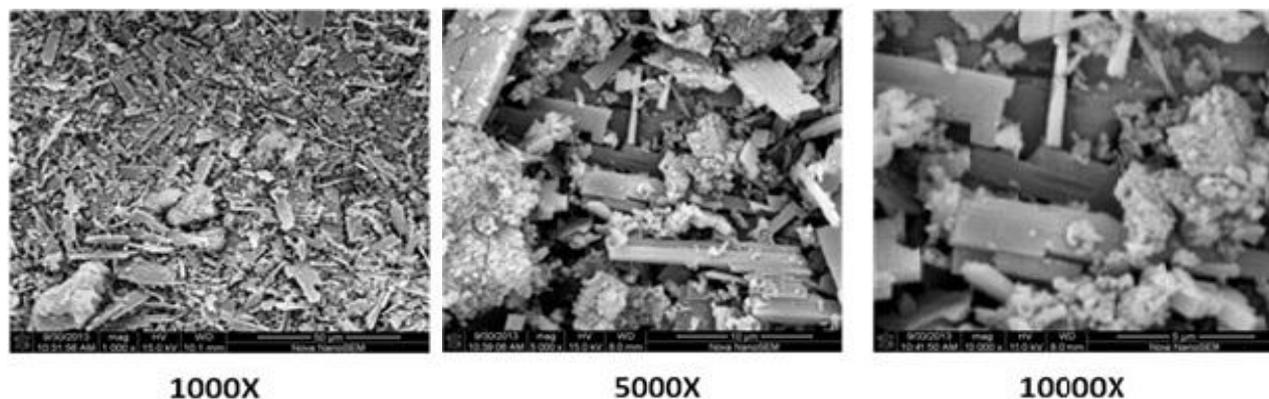


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10 **Figure 3:** Thermogravimetric curve of Gypsum produced in the laboratory.

11 3.3.4 SEM Analysis:

12 Figure 4 provides the SEM micrographs for the synthesized gypsum sample under
13 different magnifications. It can be observed that the morphology of the gypsum crystals was
14 tabular in nature as discussed by Ausset and co-workers²⁷ as well as needle shaped and rod-

1 like as discussed by Shih et al.²⁸. It can be also seen that in between the gypsum crystals
2 clusters of silica are present, as can be from the SEM microstructures at 10000X
3 magnification. This can be further confirmed from the quantitative EDS data of the material
4 as represented in table 3.



14 **Figure 4:** SEM micrographs of synthetic gypsum at three different magnifications.

15
16 Figure 5 represents an area which was examined under the EDS study. The point wise
17 analysis of this area at different points confirms the presence of silica, calcium and sulphur as
18 observed from table 3. The elemental analysis of this area of the sample can be further
19 understood as follows:

20 Points – 3 & 5 are rich in silica content and are present as clusters dispersed among the
21 tabular gypsum crystals represented by the points 1, 2, 4 & 6 which are rich in calcium,
22 sulphur and oxygen.

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Figure 5: SEM micrograph examined for EDS analysis at 10000 X magnification.

Table 3: EDS analysis for Area under study

Point No.	% O	% Si	% S	% Ca
1	31.46	2.93	30.6	35.01
2	21.38	3.02	33.74	41.87
3	24.54	24.26	25.88	25.62
4	12.74	0.91	36.69	49.66
5	13.69	45.71	21.61	18.99
6	21.77	1.31	35.45	41.47

Thus, it can be inferred that the results of the SEM-EDS analysis can be correlated and are found in complete agreement with that of the chemical composition, XRD analysis and TGA study and therefore confirm the identity of the synthetic gypsum synthesized in the laboratory.

4.0 Conclusion:

Synthetic gypsum was synthesized from LD Slag fines (-60 mesh) and was characterized by different techniques such as XRD, TGA and SEM-EDS. The characterization indicates that the synthesized material was gypsum which was evident from identification of the gypsum and anhydrite phases through XRD analysis. This observation

1 was supported by the TGA study which indicated that the synthetic gypsum is a mixture of
2 gypsum (dihydrate), hemihydrate, soluble γ -anhydrite and insoluble β -anhydrite phases of
3 gypsum. Wet chemical analysis of the material indicates that the material contains 86.12 %
4 calcium sulphate alongwith 12.52% silica. This was in accordance with the specifications for
5 the type 2 and type 3 gypsum mineral as per IS 1290:1973. The synthesized gypsum can be
6 of great value in the Portland cement industry as it can serve as an excellent replacement for
7 natural gypsum. Therefore, the present work can be envisaged as an appropriate step in
8 conservation of natural gypsum and extensive mining of the same can be reduced and
9 controlled. The present work has therefore achieved it's major objective by presenting a
10 novel route for the synthesis of a value added product (gypsum) from LD slag, which is an
11 industrial waste product of the steel industry, in an economical manner. An Indian patent
12 application bearing application number 744/KOL/2014 was also filed on the basis of this
13 study which expresses the uniqueness of the present work.

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1 **Acknowledgements:**

2 The authors are thankful to Tata Steel Management and Dr. Sanjay Chandra, Chief
3 R&D and SS for giving an opportunity to carry out the study, support and permission to
4 publish the paper. The support and services provided by staff of Chemical Laboratory,
5 Scientific Services division is also duly acknowledged.

6

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