X-RAY FLUORESCENCE BASED CHEMICAL COMPOSITION OF LADLE REFINERY FURNACE SLAG: A REVEIW

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Abstract: *This study explores different studies to find out the chemical composition of steelmaking slag generated in ladle refinery furnace. The data in this study is collected from a thorough review of the several papers in the literatures related to chemical composition of ladle refinery furnace slag. For this purpose, the paper represents data found from different study and includes data from a steelmaking plant in Bangladesh. Then an examination is carried out focusing on the chemical compositions of different slags from different corners of the world. The paper discovers the huge variation in chemical compositions of different ladle refinery furnace slags under study and the same found from different studies. It is very well clear that chemical composition greatly influences the properties of slag and the properties dictate the applications of the slag. This study has revealed the distinctive characteristic of ladle refinery furnace slag that the chemical compositions of these types of slags have lots of variations even between the batches of production in the same plant. It can also be concluded that all ladle refinery furnace slag behave very differently, depending on their chemical composition, and must be treated and studied individually. This inherent variability of ladle refinery furnace slag offers a vast area for researchers to study.*

Keywords **- Steelmaking Slag (SS), Ladle Refinery Furnace Slag (EAFS), chemical composition, X-Ray Fluorescence (XRF)**

1. INTRODUCTION

Globally various types of steels are produced through several steelmaking processes. Steelmaking processes are named according to the furnaces used in the production process. Namely open hearth (OH), basic oxygen furnace (BOF), induction arc furnace (IAF) and electric arc furnace (EAF). Steelmaking slag (SS) is a byproduct of steel making and also refining processes. To extract more of the intended material, the secondary refining of SS is done in many occasions now-a-days through ladle refinery furnaces (LRF) or ladle furnace (LF). Slag produced through this process is called secondary slag or LRF slag (LRFS) or simply LF slag (LFS) or Ladle furnace reducing slag (LFRS).

1953.304 million tonnes of crude steel was produced in 2021 only [1]. Steel use per capita in 2021 globally stands at 232.2 Per capita consumption compared to global standard indicates huge industry prospect. In 2021, 70.8% of steel were produced in BOF and 28.90% in EAF and rest 0.30% in OH process [2]. 1878 million tonnes of crude steel was produced in 2020. In 2020, it was 73.2% of steel were produced in BOF and 26.3% in EAF and rest 0.50% in OH process [3]. The statistics of 2020 and 2021 when compared show that the world steel market is growing bigger. Again the world steel industry is shifting towards EAF gradually. LRF refines the basic SS further. It is assumed that steel industry is inclining towards LRF.

Approximately 150-200 kg of SS is produced per tons of steel. It is very likely that the production amount of SS will rise in the coming years with the growth of steel production. Steel industry is unambiguously concerned about the generation of a huge quantity of this by-product, i.e. SS.

The buildup of an enormous amount of SS has caused difficulties to the steel industry due to occupation of land and harming the environment, beside the waste of resources. Moreover, factories pay so much cost for the disposal of these materials [4].

Over the last few decades, the European steel industry has focused its efforts on the improvement of by-product recovery and quality, based not only on existing technologies, but also on the development of innovative sustainable solutions. These activities have led the steel industry to save natural resources and to reduce its environmental impact, resulting in being closer to its “zero-waste” goal. In addition, the concept of Circular Economy has been recently strongly emphasized at a European level. The opportunity is perceived of improving the environmental sustainability of the steel production by saving primary raw materials and costs related to by-products and waste landfilling. [5]

Natural resources of the planet called earth are limited. Construction industry and conservation of natural resources need use of different recycled and industrial by-products in construction sector for a sustainable development of this planet. Naturally found stone is generally crushed and used as the coarse aggregate of the concrete. The objective of using SS is to replace natural aggregate in concrete as much as possible. It is initially based on its obtainability and superb physical and mechanical characteristics. SS may be utilized considerably in three main ways. The traditional practice is to dispose off SS by dumping or stockpiling on some land. Predominantly, there may be a substantial reduction in environmental pollution if SS are used up in concrete. Next, the use of SS will increase the reduction of using natural resources. Furthermore it may also contribute in guarding the energy requirements related with the natural stone processing industry. Lastly, the price of producing the concrete may be reduced.

2. PRODUCTION PROCESS OF LRFS

SS is defined as the solid material resulting from the interaction of flux and impurities during the smelting and refining of steels. The American Society for Testing Materials (ASTM) defines SS as 'a non-metallic product, consisting essentially of calcium silicates and ferrites combined with fused oxides of iron, aluminum, manganese, calcium and magnesium, that is developed simultaneously with steel in basic oxygen, electric arc, or open hearth furnaces'. [6]

Any type of SS is a molten by-product generated during the production of any type of steel. During the separation of the molten steel from impurities in steelmaking furnaces, SS is acquired. SS can be categorized according to the furnaces used for its production. LFRS is a byproduct of steelmaking industries obtained from the LF refining of carbon and low alloy steels. The ladle furnaces (LF) have only been constructed in significant numbers since the 1980's [7]. Ladle slag generation is approximately one third of the total amount of slag usually produced in an EAF [8].

The ladle furnace basic slag is produced in the final stages of steelmaking, when the steel is desulfurized in the transport ladle, during what is generally known as the secondary metallurgy process [9]. The most important functions of the secondary refining processes are the final desulfurization, the degassing of oxygen, nitrogen, and hydrogen, the removal of impurities, and the final decarburization (done for ultralow carbon steels) [10]. In the process, an average of 30 kg LFS slag per ton of steel produced [11].

LF slag is produced in the secondary metallurgy or refining process, which generates high-grade steels. In this process, liquid steel first undergoes an acid dephosphorylation process in the EAF (oxygen blowing). Then, the steel is discharged into a ladle furnace; where it is deoxidized, desulfured and alloyed under the protection of a basic slag i.e. LF Slag. [12]

The flow chart of production of LRFS is shown in the following Fig. 1.

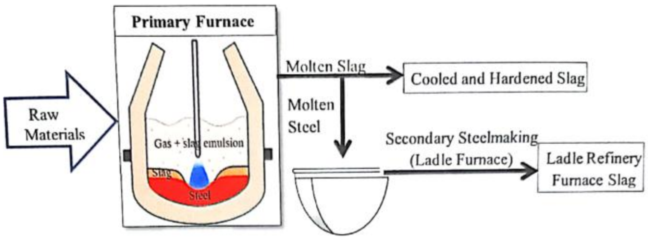

Fig - 1: Flow Chart of Production of LRFS

3. PROPERTIES OF LRFS

The properties of any type of SS define the application. So knowledge of the physical, chemical, mineralogical, and morphological properties of SS is vital. Cementitious and mechanical properties are also significant to know. Beside the mineralogical composition of SS, chemical composition has a great influence on its use for various purposes. Again, SS is a byproduct of the steelmaking process in which its quality depends on its origin [13]. The chemical, mineralogical, and morphological characteristics of SS are determined by the processes that generate this material. Therefore, knowledge of the different types of steelmaking and refining operations that produce SS as a byproduct is also required. [10]

Based on mainly, the manufacturer, types of steel generated and cooling conditions of the slag the characteristics of the SS produced differ. Furthermore, when SS are refined in ladle furnace, the properties of SS goes through another step of transformation. Thus LRFS are generated. Therefore, before any SS can be recycled into greener products or utilized or reused in different products, the study is essential to understand the slag properties. This includes how formation process of SS, its chemical compositions, mineralogical behavior, and harmful contents. The impact, abrasion and frictional properties of SS are influenced by its physical features, morphology and mineralogy. Chemistry based on chemical composition and mineralogy influences the volumetric stability of SS.

The chemical composition and cooling of molten SS have a great effect on the physical and chemical properties of solidified SS [14]. Also the rate of cooling from a molten liquid to a solid mainly affects the physical properties of SS aggregate and as such, its chemical reactivity [15]. In general, several factors are affecting physical and chemical properties of SS. These factors include: Type of steel furnace, steel making plant and SS processing [16].

4. PHYSICAL, MECHANICAL, MINERALOGICAL AND CHEMICAL PROPERTIES OF LRFS

4.1 Physical and Mechanical Properties

It was found that steel slag aggregate (SSA) has superior physical and mechanical properties as well as lower carbon footprint and reduced negative environmental effects [17, 18]. Steel slag aggregates are fairly angular, roughly cubical pieces having flat or elongated shapes. They have rough vesicular nature with many non-interconnected cells which gives a greater surface area than smoother aggregates of equal volume; this feature provides an excellent bond with Portland cement. Steel slag has a high degree of internal friction and high shear strength. The rough texture and shape ensure little breakdown in handling and construction [19].

Steel slag has high bulk specific gravity and less than 3% water absorption. Steel slag aggregates have high density, but apart from this feature most of the physical properties of steel slag are better than hard traditional rock aggregates. Below are listed some of the positive features of steel slag. [20]

LFS is obtained in a slow cooling process and presents a large content of fine particles, with 20–35% below 75 µm [21, 22]. According to its surface properties, the LFS is considered a mesoporous material with great surface area; ecotoxicity evaluations pointed out that it is a nonhazardous industrial waste [23]. LRFS has good mechanical properties: it is a crushed product with greyish or sometimes black colour stone appearance and has a very rough surface texture.

Steel slag is a dense rock having a raw density > 3.2 g/cm3 [24]. It has high abrasion resistance, low aggregate crushing value (ACV) and good resistance to fragmentation. The density of LRFS lies between 3.4-3.6 g/cm^3. It is observed that after a crushing process, the coarse aggregate can be easily adjusted to meet the grading requirements of the ASTM C33 standard (maximum size 1 in., 25 mm) [25]. LRFS found from a steel plant of Bangladesh is shown in Fig. 2.

Fig – 2: LRF Slag (LRFS)

These have a very rough surface having roughly cubical pieces with flat or elongated shapes and modestly sharp edges with numerous of pores. The angular shape helps to develop strong interlocking properties and together with the increased surface area due to cell like pores provides good bonding with cements and other aggregates. They are moderately strong and durable. It is also observed that the flakiness index value for slag was generally low which attributes to the rounded shape of SS. SS aggregate (SSA) are hard and durable and have high resistance to abrasion and impact.

4.2 Mineralogical Properties

The main mineral phases contained in SS are dicalcium silicate (C2S), tricalcium silicate (C3S), RO phase (CaO-FeO-MnOMgO solid solution), tetra-calcium aluminoferrite (C4AF), olivine, merwinite and free-CaO [26].

On the same note, the mineralogical compounds detected in the LF slag could be attributed to mayenite ($12CaO\cdot7Al_2O_3$, $Ca_{12}Al_{14}O_{33}$, and $C_{12}A_7$), periclase (MgO), gehlenite ($2CaO\cdot Al_2O_3\cdot SiO_2$, $Ca_2Al_2SiO_7$), larnite (β-$2CaO\cdot SiO_2$, β-Ca_2SiO_4), shannonite (γ-$2CaO\cdot SiO_2$, γ-Ca_2SiO_4), and tricalcium aluminate ($3CaO\cdot Al_2O_3$, $Ca_3Al_2O_6$, and C3A) [23, 27].

Cooling rate and chemical composition determine slag crystallisation [28]. The temperature at which the cooling occurs has a great influence on the final phase composition of the SS. Very rapidly cooling of the liquid slag, does not allow sufficient time for the crystals to grow. Hence crystals of the SS will be much smaller, resulting in a more homogeneous overall composition. However the rapid cooling enables the possibility of having metastable phases at low temperatures. Considering all these, LRFS are generated through slow cooling.

During the rapid cooling with water, oxidation on the surfaces may occur, and thereby the formation of soluble phases. Side by side, fast cooling will result in an abrasive surface, due to the presence of smaller grains at the surface. An abrasive surface tends to be more reactive than a plane surface, due to the increase in vapour pressure that occurs over a convex surface. Thus it will result in more grain boundaries due to the increase of small crystals in the material. Diffusion reactions are known to occur easier and faster along these boundaries [29].

4.3 Chemical Properties

The chemical behavior of SS depends on the chemical properties of SS. Similarly chemical properties of SS depend on the chemical composition which vary depending on the end materials to be produced i.e. type of steel, production process, type of furnace, feed stock i.e. raw material, cooling speed and temperature and then slag formers used to produce the steel. Besides, element of environment of the dumping place in the factory yards or any place, changes the chemical composition of the SS. Thus the raw materials used for generating steel in that locality and exposure of SS to ambience of the specific locality greatly contribute in changing the chemical composition leading to its chemical properties.

The main components of the LFS are calcium, silicon, magnesium, aluminum oxides, and calcium silicates under various allotropic forms [30]. The main compounds are calcium, silicon, magnesium, and aluminum oxides representing more than 92% of the total mass [23]. Other minor components include other oxidized impurities, such as MnO and SO_3.

The chemical composition and mineral phase types of SS from diverse generating areas and plants may be different depending on the differences in steelmaking raw materials and smelting processes. The LRF steelmaking process is fundamentally an additional step to basic steelmaking process. Again the chemical composition of SS depends on the steelmaking process which is also an important factor for its CO_2 reactivity [21]. The composition of the Iron-bearing feed i.e. the raw materials and the batch nature of the steelmaking practices can introduce even larger variation. It is significant that LRFS composition is dependent on the raw material source for the basic furnace and its chemistry may differ from one batch to another. For LRFS cooling temperature and rate play a vital role. It is worth mentionable that cooling rate and chemical composition regulate slag crystallization.

5. CHEMICAL COMPOSITION OF DIFFERENT LRFS

It is predicted that LRFS from different parts of the world and different producers of steel may exhibit a different appearance, physical and chemical properties, depending on the composition of steel scrap that is used as feed materials, the type of furnace, steel grades, refining and cooling processes. The characteristics of the slag produced at each steel manufacturing plant may vary because it depends on the entire production process of steel used from feeding raw materials up to the SS dumped. The feature, quality and composition of LRFS depend on the steel scrap used as raw material, type and share in the heat of specific nonmetallic supplements, type of steel produced, type of furnace used and other technological parameters including rate and temperature of cooling.

Review of several studies found out some factors on which the properties of the SS depend. These are namely the furnace type and condition, source, type and chemical composition of steel scrap and other raw materials, type of process (batch process in which reactions are not always completed, thus resulting in a non-uniform slag), use of Dolomite, types of steel produced, type and rate of cooling, temperature at which cooled, weathering effect, age of the SS, hazardous contents etc. All these factors are applicable for LRFS also. Analyses of investigated slag by EDS have determined that CaO content was 19.02-51.34%, SiO_2 (11.3–30.1%), Al_2O_3 (8.54–15.18%), MgO (7.66–18.84%), FeO (1.17–7.45%), MnO (0.22–1.34%), Cr_2O_3 (0.04–0.92%), P_2O_5 (1.52–3%), TiO_2 (0.08–0.22%), K_2O (0.19–1.68%) and Na_2O (0.38–0.56%) [27].

Fig. 3 shows an X-ray Fluorescence (XRF) spectrometer made in UK.

Fig – 3: Thermo Scientific ARL QUANT'X XRF Spectrometer

Fig. 3 shows the ARL QUANT’X which is a compact high-performance Energy Dispersive XRF (EDXRF). It was used to obtain the chemical compositions of the LRFS collected from a steelmaking plant of Bangladesh.

X-ray fluorescence (XRF) is the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by being bombarded with high-energy X-rays or gamma rays. The phenomenon is widely used for elemental analysis and chemical analysis, particularly in the investigation of metals, glass, ceramics and building materials, and for research in geochemistry, forensic science, archaeology and art objects. [33]

The chemical composition of LRFS is most commonly investigated using XRF spectroscopy. It may be well-defined by different oxides present in LRFS. Mainly oxides like CaO, Al_2O_3, SiO_2, MgO, Fe_2O_3, FeO, MnO, P_2O_5, TiO_2, MnO_2, SO_3, Cr_2O_3, Na_2O, K_2O, TiO_2, Free MgO and Free CaO etc. remain present in LRFS. Beside there may be also other several oxides, metallic or nonmetallic chemical elements i.e. S, C, P, Cr, Zn and F. Now comparisons of some constituents of the LRFS from different parts of the world are described in the following paragraphs.

Unlike natural stone, steel slag contains excess free calcium oxide (f-CaO) or/and free magnesium oxide (f-MgO) on its surface. Free lime, with a specific gravity of 3.34, can react with water to produce $Ca(OH)_2$, with a specific gravity of 2.23, which results in volume expansion [31]. Steel slag grains expansion can be caused by lime hydration and carbonation and magnesia hydration and carbonation [32]. So it is worth noting that this SS may be subjected to volumetric instability problems. Same is the case with LRFS.

Some aspects contribute to the presence of free lime and periclase, dealing particularly with the steelmaking process and to the slag cooling, from the heated furnace to environmental temperature at the dumping place. The existence of free lime and periclase (MgO) in SS affects the characteristics of it.

In the case of SS, the slag contains metallic elements such as iron in oxide form; however, because refining time is short and the amount of limestone contained is large, a portion of the limestone auxiliary material may remain un-dissolved as free CaO [16].

The main chemical components found in LRFS are considered whose highest mass ranges more than 2% are listed below. There are total 12 oxide elements, i.e. CaO, SiO_2, MgO, MnO, FeO, Fe_2O_3, Al_2O_3, Free Lime (CaO), SO_3, P_2O_5, MnO_2 and Free MgO are significantly found in LRFS. These elements together make about 98% of the total composition. A summary of these elements found from 30 different studies carried out in 13 countries are shown in the following Table 1.

Table - 1: Chemical Composition of LRFS (% by Mass of Main Constituents)

Ser	Source	Chemical Composition of LRFS (% by Mass of Main Constituents)											
		CaO	SiO_2	MgO	MnO	FeO	Fe_2O_3	Al_2O_3	Free CaO	SO_3	P_2O_5	Free MgO	MnO_2
1	Australia [34]	52.50		9.99	0.39	0.55		2.50			17.50		
2	Melbourne, Australia [35]	24.90	22.93	8.66			35.23			0.50	0.47		5.83
3	Chattogram, Bangladesh [36]	53.19	27.96	6.79	0.70	2.11							
4	Chattogram, Bangladesh [37]	32.56	14.92	9.34	4.76	17.27		9.56			0.42		
5	Chattogram, Bangladesh [38]	44.35	27.32	12.43	1.48	6.13		5.84			0.23		
6	South West Brazil [39]	60.85	30.65	7.30	0.90		2.65	2.45			0.25		
7	Hamilton, Ontario, Canada [7]	50.00	6.00	9.00	1.80	2.80		29.00			0.40		
8	Hamilton, Ontario, Canada [14]	45.00	18.50	5.50	2.50	7.50		20.00		0.55	0.25		
9	Ontario, Canada [40]	65.23	12.35	3.96			0.79	16.55					
10		57.55	6.21	5.04			3.55	23.17					
11	China [41]	49.50	19.59	7.40	1.40		0.90	12.30	2.50		0.40		
12	Sisak, Croatia [23]	48.37	15.00	15.25		1.54		14.30			2.73		
13	Greece [42]	55.73	24.10	5.93			1.60	1.53	0.77				
14	India [7]	52.50	4.50	9.00	0.10	1.00		30.00			<0.1		
15	India [43]	50.40	5.90	8.50	0.10	1.00		32.00					

16	Romania [24]	40.78	17.81	8.53	9.79	9.25	3.97	4.23			0.74		
17		49.56	14.73	7.88	0.39	0.44	0.22	25.55			0.20		
18	Russia [44]	70.10	15.01	10.05	0.43	0.54		3.64					
19	Revda, Sverdlovsk, Russia [45]	58.07	24.45	8.27	0.24	1.12		6.86					
20	Magnitogorsk, Chelyabinsk, Russia [45]	50.39	14.32	8.89	3.71	8.06		14.64					
21	Nizhny Tagil, Sverdlovsk, Russia [45]	52.66	18.39	7.64	0.36	0.66		20.29					
22		59.07	12.80	4.89	0.46	0.15		22.63					
23	Spain [11]	58.00	17.00	10.00				12.00		1.00	1.50 (with others)		
24	Spain [46]	56.70	17.70	9.60			2.20	6.60		0.86	0.01		
25	Spain [47]	54.00	14.3	16.50			1.77	10.30	5.00			14	
26	Spain [12]	55.79	23.5	6.00			1.69	4.29					
27	Sweden [29] [48]	42.50	14.20	12.60	0.20	0.50	1.10	22.90					
28	US and Canada [14]	45.00	18.5	5.50	2.5	7.55		20					
29	US and Canada [49]	49.43	12.96	6.23	1.06	5.61							
30	Crawfordsville, Indiana, USA [10]	47.52	4.64	7.35	1.00	7.61		22.59		2.30	0.09		

The chemical compositions (%) by mass found in highest 2% are listed below. There are total 11 elements, i.e. S, C, Na_2O, K_2O, TiO_2, Cr, Cr_2O_3, Zn, ZrO_2, P and F are seen to be scantily found in SS. A summary of these elements found from the above mentioned 30 studies are shown in the following Table 2.

Table - 2: Chemical Composition of LRFS (% by Mass of Minor Constituents)

Ser	Source	Chemical Composition of LRFS (% by Mass of Minor Constituents)										
		Cr_2O_3	Na_2O	K_2O	TiO_2	ZrO_2	S	C	P	Cr	Zn	F
1	Melbourne, Australia [35]	0.95		0.06	0.50							
2	Chattogram, Bangladesh [37]	1.59					0.07					
3	Chattogram, Bangladesh [38]	0.14					0.34					
4	South West Brazil [39]	0.90										
5	Hamilton, Ontario, Canada [7]						0.50					
6	Sisak, Croatia [23]	0.92	0.43	0.36	0.20							
7	Greece [42]		0.60	0.30								
8	India [7]						0.50		<0.1			
9	India [43]						0.50		<0.1			
10	Romania [24]	1.42					0.30	0.64				
11	Romania [24]						0.80	0.07				
12	Spain [11]	1.5 (with others)										
13	Spain [46]				0.60							
14	Spain [47]			<0.1			1.50					

15	US and Canada [14]						0.55		0.25	0.25		
16	US and Canada [49]	0.25	0.01	0.01	0.34		1.33	0.38	0.08			1.66
17	Crawfordsville, Indiana, USA [10]	0.37	0.06	0.02	0.33	0.20					0.01	

*Studies did not find any trace of the above elements is not shown in the table.

6. DISCUSSIONS

The main chemical constituents of LRF slags can vary widely. Based on the review of the 30 studies, the CaO, SiO_2, MgO, MnO, FeO, Fe_2O_3, Al_2O_3, Free Lime (CaO), SO_3, P_2O_5, Free MgO and MnO_2 contents of LRF slags are in the 24.90–70.10%, 0–30.65%, 3.96–16.50%, 0–9.79%, 0-17.27%, 0-35.23%, 0-32%, 0-5%, 0-2.30%, 0-17.50%, 0-14% and 0-5.83% ranges, respectively. The widest range (45.20) was found with the CaO and the narrowest one (2.30) is the SO_3. It shows CaO and MgO are the common main constituents of LRFS in all the 30 studies. Maximum 8 elements are found in the studies of China [41], India [7], Romania [24] and USA [10] each.

From the studies, the highest CaO% was found in the LRFS of a study carried out in Russia [44]. Besides the lowest CaO% was found in the LRFS of a study carried out in Australia [35]. Free Lime (CaO) was found in LRFS of China [41] and Spain [47] significantly and very scantily in Greece [42]. It is mentionable that the volume expansion of SS depends predominantly on Free Lime (CaO).

MgO also contributes to expansion of SS [34]. The swelling potential of steel slag is of particular importance because of the free lime or magnesia in the slag [50]. The highest MgO% was found in the LRFS of a study carried out in Spain [47]. Besides the lowest MgO% was found in the LRFS of a study carried out in Canada [40]. Free Lime (MgO) was found only in the LRFS of Spain [47] significantly and very scantily in Spain [11]. MgO which is one of the two common constituents, regulates and manages the crystallization, and further improves the sintering characteristics. It also increases porosity and bending strength of LRFS.

The key factor prescribing slag use is the alkaline-earth metal (e.g., Ca and Mg) oxide contents, which contribute to overall basicity and cementitious strength. However, as-produced steelmaking slag is chemically unstable as these oxides readily form hydroxides and carbonates through reaction with atmospheric gases. Both hydroxide and carbonate formation produce substantial mechanical swelling, leading to heave failure in confined construction applications. [51]

The highest SiO_2% was found in the LRFS of a study carried out in Brazil [39]. Besides No trace of SiO_2% was found in the LRFS of a study carried out in Australia [34]. SiO_2 increases mechanical strength of the LRFS. SO_3 was found in the LRFS studied in Bangladesh, Croatia, Egypt, Romania and USA. Steel slag contains a lot of metal elements such as calcium oxide (CaO) and silica and has good compressive performance [52].

The highest MnO% was found in the LRFS of a study carried out in Romania [24]. No MnO trace was found in LRFS in the studies of Australia [35], Canada [40], Croatia [23], Greece [42] and Spain [11, 12, 46, 47]. MnO shows high adsorption ability of any compound element.

The highest FeO% found in LRFS in Bangladesh [37] is 17.27%. No trace of FeO was found in the SS of Australia [35], Brazil [39], Canada [40], China [41], Greece [42] and Spain [11, 12, 46, 47].

Fe_2O_3 increases specific capacity, density, electro-chemical properties and mechanical performance, but reduces pore size. The high iron oxide content of the aggregate results in very hard and very dense aggregate (20-30% heavier than naturally occurring aggregates such as basalt and granite) [53]. The highest Fe_2O_3 found in LRFS in Australia [35] is 17.27%. No trace of Fe_2O_3 was found in the SS of Australia [34], Bangladesh [36, 37, 38], Canada [7, 14], Croatia [23], Russia [44, 45], Spain [11] and USA [10].

Again, the highest Al_2O_3% was found in the LRFS of a study carried out in India [43]. No trace of Al_2O_3 was found in LRFS of studies in Australia [35], Bangladesh [36], USA and Canada [49]. It removes most of the oxygen in the SS to produce deoxidized steel. Deoxidization provides abrasive property through hardness. It also provides strength through densification and mechanical strength.

SO_3% was significantly found only in LRFS in Australia [35], Canada [14], Spain [11, 46] and USA [10]. It may contribute to the expansive performance of LRFS.

The highest P_2O_5% found in LRFS in Australia [34] is 17.50%. No trace of P_2O_5 was found in the SS of Bangladesh [36], Canada [40], Greece [42], Russia [44, 45], Spain [12, 47], Sweden [29, 48] and USA [14, 49]. P_2O_5 increases thermal stability, conductivity, and mechanical flexibility in a composite material. It might also show some hazardous characteristics when present in the LRFS.

MnO_2 in a good percentage was found in a study carried out on SS of Australia [35] only. A trace was found in a study carried out in Spain [11]. Some of the known heavy metals that might be present in LRFS are Cr and Zn. Although these heavy metals often appear only as trace elements, they serve as key factors in pollution and toxicity [53].

If country wise averages are anyway considered, following Table 3 refers to the averages of the elements significantly found in LRFS.

Table - 3: Chemical Composition of Main Constituents of LRFS (% of Average Mass)

Serial	Source Country	Chemical Composition (% of Average Mass) of Main Constituents										
		CaO	SiO_2	MgO	MnO	FeO+ Fe_2O_3	Al_2O_3	Free CaO	SO_3	P_2O_5	Free MgO	MnO_2
1.	Australia	38.70	11.47	9.33	0.20	17.89	1.25		0.25	8.99		2.92
2.	Bangladesh	43.37	23.40	9.52	2.32	8.51	5.14			0.22		
3.	Brazil	60.85	30.65	7.30	0.90	2.65	2.45			0.25		
4.	Canada	54.45	10.77	5.88	1.08	3.66	22.18		0.14	0.17		
5.	China	49.50	19.59	7.40	1.40	0.90	12.30	2.50		0.40		
6.	Croatia	48.37	15.00	15.25		1.54	14.30			2.73		
7.	Greece	55.73	24.10	5.93		1.60	1.53	0.77				
8.	India	51.45	5.20	8.75	0.10	1.00	31.00			0.05		
9.	Romania	45.17	16.27	8.21	5.09	6.94	14.89			0.47		
10.	Russia	58.06	17.00	7.95	1.04	2.09	13.62					
11.	Spain	56.13	18.13	10.53		1.42	8.30	1.25	0.47	0.38	3.88	0.38
12.	Sweden	42.50	14.20	12.60	0.20	1.60	12.90					
13.	USA	47.52	4.64	7.35	1.00	7.61	12.59		2.30	0.09		

The Table 3 shows, when considered country wise, CaO, SiO_2, MgO and Al_2O_3 are found in any of the study on LRFS in all the 13 source countries.

The Fig. 4 below gives a representation of the Table 3 showing the only the most common oxides of LRFS found commonly amongst the countries where studies were conducted.

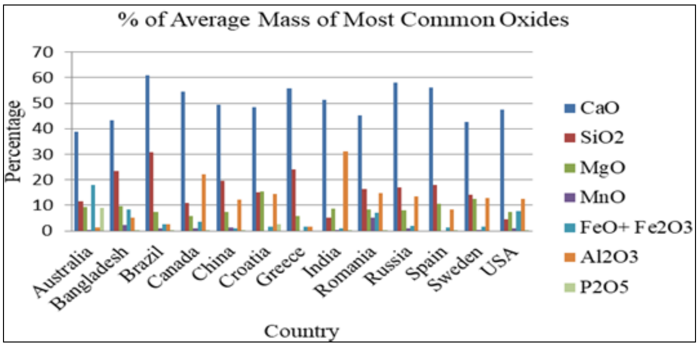

Fig – 4: Chemical Compositions of Most Common Oxides of Country wise LRFS (% of Average Mass)

According to the averages shown in Table 3, the CaO, SiO_2, MgO, FeO+Fe_2O_3 and Al_2O_3 are common among the 13 countries. In Spain, ten oxides out of eleven shown in the Table 3 are found except MnO. The main constituents of LRFS in Spain are shown in the Fig. 5.

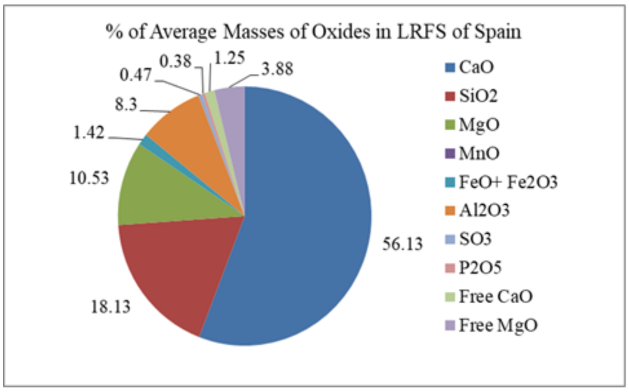

Fig – 5: Percentages of Average Masses of Oxides Found in LRFS of Spain

Again except Free CaO and Free MgO, nine oxide elements were found in LRFS of Australia. The main constituents of LRFS of Australia are shown in the Fig. 6.

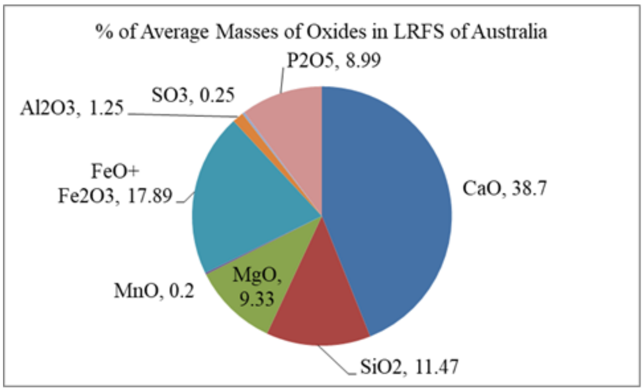

Fig – 6: Percentages of Average Masses of Oxides Found in LRFS of Australia

It is noteworthy that EAFS composition is dependent on the raw material source and its chemistry can vary from one batch to another. The rate of cooling from a molten liquid to a solid mainly affects the physical properties of SS and as such, its chemical reactivity [15]. Same is the case with LRFS.

Based on the studies the ranges of Cr_2O_3, Na_2O, K_2O, TiO_2, ZrO_2, S, C, P, Cr, Zn and F and are 0-1.59%, 0-0.60%, 0-0.36%, 0-0.60%, 0-0.20%, 0-1.50%, 0-0.64%, 0-0.25%, 0-0.25%, 0-0.01% and 0-1.66% respectively.

The highest Cr_2O_3% was found in LRFS in Bangladesh is 1.59% [37]. However, no trace of Cr_2O_3 was found in the LRFS of Bangladesh [36], Canada [7], China [41], Greece [42], India [7, 43], Russia [44, 45], Spain [46, 47] and Sweden [29, 48]. Cr_2O_3 may be the responsible oxide for the color of the LRFS when present. It may also provide some resistance to acid.

Some traces of Na_2O were found in the LRFS of a study carried out in Croatia [23], Greece [42], Spain [11], USA and Canada [14]. However the highest percentage was 0.60% in Greece [42]. No trace of Na_2O was found in the LRFS of Australia [34, 35], Bangladesh [36, 37, 38], Brazil [39], Canada [7, 14, 40], China [41], India [7, 43], Romania [24], Russia [44, 45] and Sweden [29, 48]. Na_2O may control the crystallization, and further develops the sintering features and also increases porosity in a composite material.

The highest trace of K_2O in percentage of total mass was found in the LRFS of a study carried out in Croatia (0.36%). No trace of K_2O was found in the LRFS of Bangladesh [36, 37, 38], Brazil [39], Canada [7, 14, 40], China [41], Romania [24], Russia [44, 45] and Sweden [29, 48]. It improves densification and mechanical strength of a composite material.

TiO_2 traces were found in the studies in Australia [35], Croatia [23], Spain [11, 46] and USA [10] and Canada [49] only. It may increase the surface area, specific capacity, adsorption efficiency and electro- chemical properties of LRFS. The highest TiO_2% was found in the LRFS of a study carried out in Spain (0.60%) [46]. No trace of TiO_2 was found in the LRFS of Bangladesh [36], Brazil [39], Canada [7, 14, 40], China [41], Greece [42], India [7, 43], Romania [24], Russia [44, 45] and Sweden [29, 48]. It may help in crystallization, viscosity, and mechanical properties of a composite material.

ZrO_2 traces were found in LRFS of Spain [11] and USA [10] only. The highest trace was 0.20% in the study of USA. ZrO_2 may improve the microstructure properties and solubility. Again it may protect the composite structure from crack propagation.

S traces were found in the LRFS of Bangladesh [37, 38], Canada [7], India [7, 43], Romania [24], Spain [11, 47] and USA and Canada [14, 49]. No traces of S were found in Australia [34, 35], Brazil [39], China [41], Croatia [23], Greece [42], Russia [44, 45] and Sweden [29, 48].

C traces were found in the LRFS of Romania [24], Spain [11] and USA and Canada [49] only. P traces were found in the LRFS of India [7, 43], Spain [11] and USA and Canada [14, 49] only.

Cr traces were found in the LRFS of Spain [11] and USA and Canada [14] only. Cr is responsible for enhancing mechanical performance (tensile strength), interfacial bonding strength, and thermal conductivity of LRFS. Zn traces were found in the LRFS of Spain [11] and USA [10] only. F traces were found in the LRFS of USA and Canada [49] only. Compressive strength of LRFS may decrease with increasing F content.

Country wise averages of minor elements found in LRFS are presented in the following Table 4.

Table - 4: Chemical Composition of Minor Constituents of LRFS (% of Average Mass)

Serial	Source Country	Chemical Composition (% of Average Mass) of Minor Constituents										
		Cr_2O_3	Na_2O	K_2O	TiO_2	ZrO_2	S	C	P	Cr	Zn	F
1.	Australia	0.48		0.03	0.25							
2.	Bangladesh	0.58					0.14					
3.	Brazil	0.90										
4.	Canada						0.13					
5.	Croatia	0.92	0.43	0.36	0.20							
6.	Greece		0.60	0.30								
7.	India						0.50		0.10			
8.	Romania	0.71					0.40	0.36				
9.	Spain	0.03	0.03	0.03	0.04	0.03	0.06	0.03	0.03	0.03	0.03	0.03
10.	USA	0.37	0.06	0.02	0.33	0.02					0.01	

*Studies did not find any traces of the above elements in any of the countries are not shown in the Table 4.

In a graphical representation of the Table 4 would show as the Fig. 7 below.

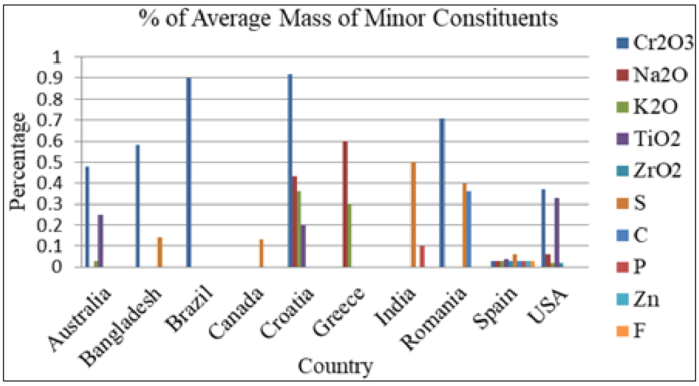

Fig – 7: Chemical Compositions of Minor Constituents of LRFS (% of Average Mass)

Based on the averages of Table 4, all the ten elements were found in the LRFS studied in Spain, though in very less percentages. Cr_2O_3, Na_2O, K_2O, TiO_2, ZrO_2, S, C, P, Cr, Zn and F traces are found in LRFS of Spain. Cr_2O_3, Na_2O, K_2O, TiO_2, ZrO_2 and Zn are found in the LRFS of USA. These are shown in the Fig. 8.

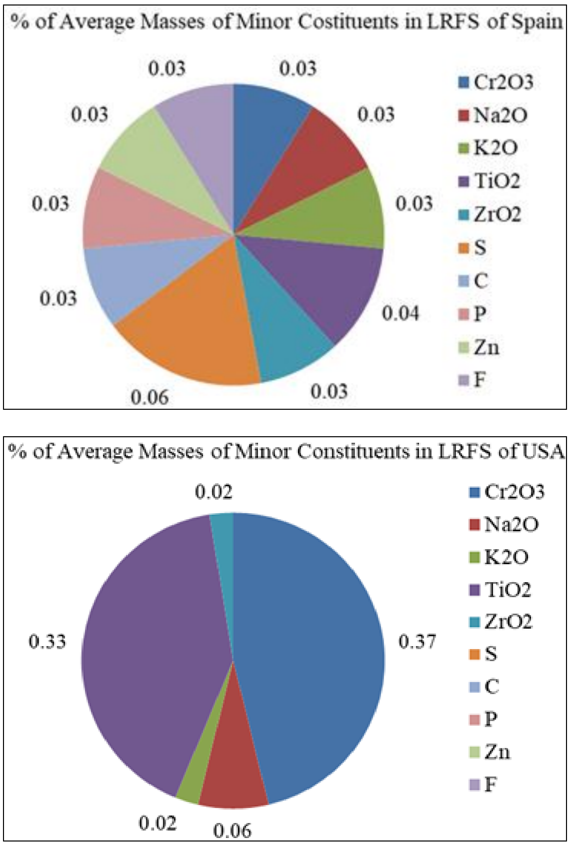

Fig - 8: Percentages of Minor Constituents of LRFS in Spain and USA

7. CONCLUSIONS

Formerly considered waste material, steel slag has become a valuable by-product used as a raw material for many industries and is almost fully utilized in some countries [54]. The production of the huge amount of LRFS as co-products of steelmaking operations has become a great concern for the steel industry. The amassing of a huge volume of LRFS has caused and causing several problems also every day. If LRFS are suitably used, problems of steel industry would be reduced to a bearable one.

This paper summarizes the findings assimilated from a wide-ranging literature review focused on the chemical compositions related to different types of LRFS as well as recognizing corresponding areas of study for future viewpoints. The broad review implies that the variations of the LRFS are based on the important differences in chemical compositions of LRFS. It is obvious that different types of chemical compositions result in different properties of LRFS. This also has a pronounced impact on the utilizations of LRFS.

LRFS is a compound material of silicates, oxides and some elements that solidifies during cooling. There is characteristically a huge variation in the physical, chemical, and mineralogical properties of all types of LRFS being generated in different corners of the world. This difference depends on the steel-making plant, steel-making process, raw materials of the plants, and types of furnace, processing, the grade of steel produced, storage strategies and type, speed, rate and temperature of cooling etc. Further to add, LRFS may depend on the primary slag produced which is further refined. For this reason, the behaviors and characteristics of LRFS is very different from one to another. Thus LRFS must be considered with credit of the inherent variability as its uniqueness.

Moreover the chemical composition of LRFS varies from country to country and even within the same country region to region and further due to the each and every single factor related with the production system. The dissimilarity is for the differences in the composition of raw materials used, for the differences of types of furnaces used or in operating procedures in batching or in others in the plant also. Thus variations can even be seen from factory to factory, plant to plant and even batch to batch. Even the ambience influences in producing slag.

It can also be concluded that all LRFS perform very differently, depending on their chemical composition, and must be treated and studied individually. This inherent variability of LRFS offers a huge area for researchers to study. This vast research field may be explored and studied thoroughly and methodically to use LRFS in all the ways possible for the development of the human civilization. Hence it can be said that LRFS warrants independent research on each and every type of it.

Lastly the review conducted on the different kinds of LRFS studied by several researchers can be concluded like this. Considering the variations of the chemical compositions of LRFS, each type of LRFS requires a separate research to be able to understand the chemical characteristics of LRFS and related engineering properties for its applications in the desired fields.

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