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Industrial waste produced in the UAE, valuable high-temperature materials for thermal energy storage applications

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Abstract

Several industrial waste from metal industries in the UAE have been identified to be recycled as low-cost materials for high-temperature thermal energy storage (TES) systems development. Electric arc furnace (EAF) slag, ladle furnace (LF) slag, aluminum pot skimming (APS) and aluminum white dross (AWD) have been chemically and thermally characterized. Chemical analysis showed that these materials contain relatively inert components and are non-hazardous in general (neglected amount of heavy metals). In addition, except for APS, these wastes were in general stable at high temperatures up to 1100 °C after performing one or two thermal cycles.

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Keywords: Thermal energy storage (TES); high-temperature; industrial waste; furnace slags; aluminum dross; pot skimming

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1. Introduction

Concentrated solar power (CSP) technology has an advantage by been dispatchable contrary to other renewable energy technologies such as wind or photovoltaic. Integrating thermal energy storage (TES) system in CSP plants contributes in decreasing the levelized cost of energy (LCOE) and makes CSP more reliable and economically profitable on the renewable energy market. Therefore, innovative high-temperature TES systems based on inexpensive materials are required. These new TES materials should be among others: inexpensive, available in large quantity, thermally and chemically stable up to high temperature (1000 °C), and compatible with heat transfer fluids.

Masdar Institute of Science and Technology is proposing an innovative approach in the United Arab Emirates (UAE), which consists of recycling locally produced industrial waste as TES materials. This approach has been successfully validated in Europe with ceramic coming from treatment of asbestos containing waste [1 - 4], municipal solid waste incinerator fly ash [5], coal ash from thermal power plants [6] and more recently with black slags from steel industry [7 - 8]. These glass/ceramic materials, mainly composed of metal oxides, have all demonstrated relevant properties to store thermal energy by sensible heat from ambient temperature up to 1000 °C. This noble solution is believed to result in a significant reduction in storage system cost and would avoid large importation of thousand tons of conventional storage material (e.g., nitrate salts from Chile). Additionally, by finding a way to recycle those waste that are usually landfilled, their environmental impact would be lowered.

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Industrial wastes from metal industries have been identified to study their recycling potential as high-temperature TES materials. As per 2013 statistics, the world steel and aluminum production were more than 127 million tons [9] and around 43 million tons [10], respectively. A considerable amount of waste is engendered by these industries everywhere in the world. For example, in the USA, steel industries generate 10 to 15 million tons of steel slag every year [11]. In the UAE, around 10 million tons of metal was produced in 2014 causing large amount of waste. Therefore, different industrial waste produced by two large metal companies; Emirates Aluminium (EMAL) and Emirates Steel, have been identified. Large quantity of furnace slags, aluminum dross, pot skimming, spent pot lining, and carbon dust are generated yearly by these two companies. Most of those wastes are currently stored on site without any revalorization as landfilling is totally prohibited in the UAE. In this work, some samples have been characterized to be reused as low-cost and sustainable TES materials in high-temperature applications. The first step in material characterization was to relate their chemical composition and thermal stability.

Nomenclature

APS	Aluminum pot skimming
AWD	Aluminum white dross
CSP	Concentrated solar power
EAF	Electric arc furnace
EDS	Energy dispersive X-ray spectroscopy
EMAL	Emirates Aluminium
FTIR	Fourier transform infrared spectrometer
LCOE	Levelized cost of energy
LF	Ladle furnace
SEM	Scanning electron microscope
STA	Simultaneous thermal analyser
TES	Thermal energy storage
TGA	Thermal gravimetric analyser
UAE	United Arab Emirates
XRF	X-ray fluorescence

2. Materials Selection

In this work, four types of samples were selected and examined. The first two are (0 - 5 mm) electric arc furnace (EAF) slag and ladle furnace (LF) slag from steel industry, (see **Fig. 1** a and b).

EAF slag is produced during steel manufacturing process using EAF technology and is tapped from slag door by tilting the furnace. The formation of liquid EAF slag on the top of the molten bath removes the non-metallic scrap components and the steel incompatible elements, which results in a higher quality of metal. In addition, the slag is functioning as a protective layer preserving the molten bath from any further oxidation. Simultaneously, this layer maintains the temperature of the bath through a kind of lid formation during all the process.

The LF slag is generated as a by-product in the secondary refining process of the molten steel in ladle furnace. It has an important role in final steel desulphurization, degassing, impurities removal and decarburization.

The other two samples are aluminum pot skimming (APS) and aluminum white dross (AWD) from aluminum industry, (see **Fig. 1** c and d). In aluminum production, carbon anodes are consumed during reduction process of alumina (Al_2O_3) and a floating layer is formed on the top of the molten bath, which consists of carbon dust and some bath contents, i.e. alumina (Al_2O_3) and cryolite (Na_3AlF_6). This layer termed as APS, is skimmed before tapping the molten metal. AWD is generated in casting operations. When molten aluminum is alloyed with different elements and due to oxidation, AWD layer floats on the surface of the molten aluminum.

Fig. 1. (a) EAF slag; (b) LF slag; (c) APS; (d) AWD as-received samples

3. Characterization methods

The elemental analysis of each sample was carried out by energy dispersive X-ray spectroscopy (EDS) equipped on a scanning electron microscope (SEM) Quanta 250 (FEI). Chemical elements of powder samples were also characterized using X-ray fluorescence (XRF), Niton XL3 XRF from Thermo scientific. The AWD powder was obtained by first crushing the raw sample with Mortar and pestle. Then it was grinded using Planetary Ball Mill PM100 from Retsch. For EAF slag and APS, a mixture of powder and tiny particles in the bottom of the container was separated and sieved using sieves with different mesh sizes. LF slag is already a powder.

Routine thermal gravimetric analyser (TGA) tests were performed with a simultaneous thermal analyser (STA) 449 F3 Jupiter from Netzsch Company to study the thermal stability from ambient temperature up to 1100 °C. This tool is coupled to a Fourier transform infrared (FTIR) spectrometer Vertex 80v from Bruker Optics Company to analyse the decomposed gases. Two thermal cycles have been performed on the as-received samples. The first cycle was heating from 40 °C to 1100 °C. The sample was left at 1100 °C for 20 minutes then cooled down to 100 °C. Another heating cycle up to 1100 °C was performed thereafter.

4. Experimental results

4.1. Chemical Composition

4.1.1 EDS

EDS spectrums of as-received samples are presented in **Fig. 2**. An intense peak for nitrogen appeared in EAF slag spectrum. This is expected knowing the significant role of nitrogen in enhancing the mechanical properties of steel and also due to the inevitable air trapping during the manufacturing process. The chemical analysis of both EAF slag and LF slag revealed the presence of peaks for Fe, Ca, O and Si beside traces of other elements such as Mg, Mn and B. However, a higher amount of iron has been found in EAF slag. This is expected as a result of the different sources and manufacturing process for these two types of slag [11].

Additionally, APS and AWD spectrums both showed a high peak of Al and minor peaks of impurities. The types of impurities found in AWD can vary depending on the alloying elements used to produce the finished product. The presence of important quantities of C, F and Na is attributed to the source of APS, i.e. a floating layer on the top of the molten bath in reduction process.

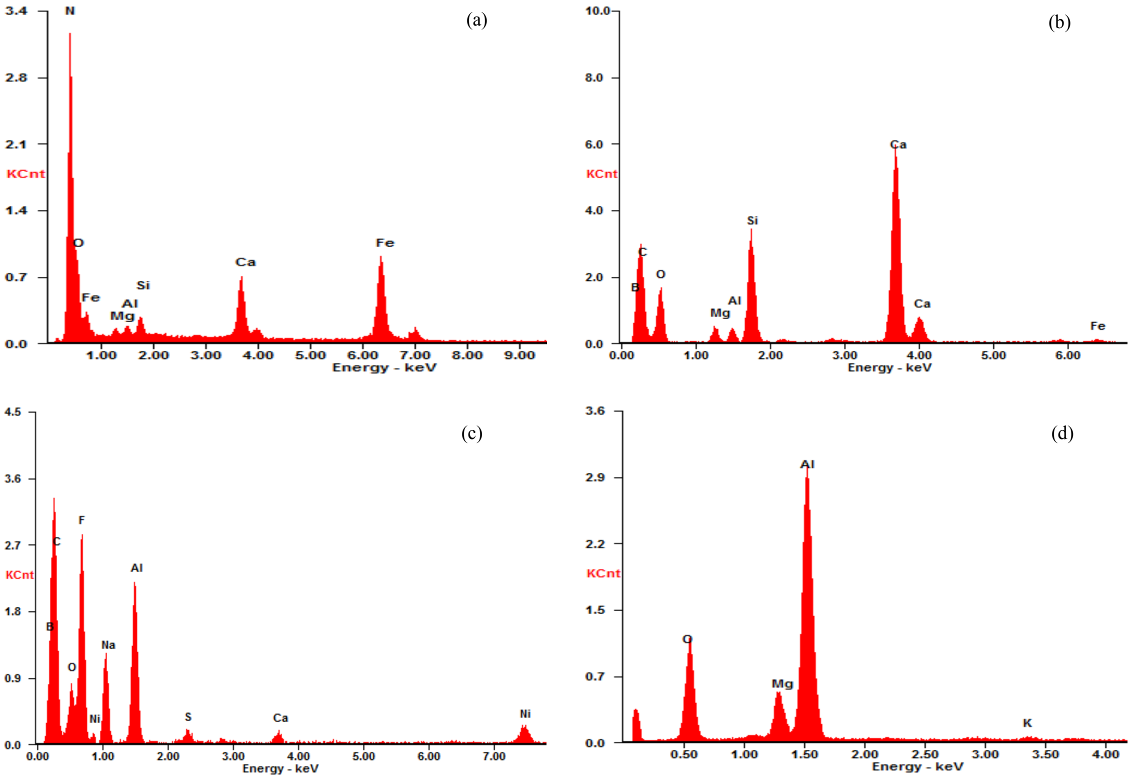

Fig. 2. EDS spectrums of (a) EAF slag; (b) LF slag; (c) APS; and (d) AWD as-received samples.

4.1.2 XRF

The XRF chemical analysis (**Table 1**) confirmed that EAF slag sample contains a high amount of Fe (~20 %) and a lower amount is found in LF slag. A quantifiable mass fraction for calcium (higher in LF slag) appears in the analysis. This results from using lime (CaO) and/or dolomite ($MgCa(CO_3)_2$) as fluxing agent. In addition, both steel slags have significant amount of silicon. Sources of Si are recycled steel scrap used to feed the EAF and desulfurizing agents and deoxidation process in LF refining [11]. Steel slags are composed mainly of metal oxides but due to the limitation of the Niton XL3 XRF tool, we did not detect light elements (with atomic number (Z=11) and lower). The mass fraction of light elements is contained in Bal* in the table.

About 80 % of mass fraction is accounted for light elements for APS, which is expected knowing that APS composed mainly of carbon. A significant mass fraction of free Al metal (~28 %) is found in AWD sample. This is the reason behind reprocessing AWD by aluminum smelters to reclaim as much as possible of the Al metal. Another point to mention here is that the mass fraction of Fe in AWD is due to two main reasons: (1) alloys used in finished product and (2) steel balls used in the milling bowl to obtain the powder sample. The mass fraction of light elements for AWD is accounted mainly for oxygen since AWD composes mainly of metal oxides as in literature [12]. In addition to the elements shown in **Table 1**, small traces of other elements are found in the four samples.

Table 1. XRF Analysis of EAF slag, LF slag, APS, AWD. (*Balance: represent the light elements in the sample)

Weight %	Fe	Si	Al	Ca	Bal*	S	Mg	Ti	Ni	Cr	Mn	Cl	K	As
EAF slag	20.22	10.37	1.50	24.10	41.81	0.32	-	0.15	-	-	0.84	0.34	0.14	-
LF slag	2.69	16.11	1.79	36.39	40.87	0.15	-	0.17	-	-	1.70	-	-	-
APS	0.61	2.70	4.84	4.07	82.29	2.88	-	-	2.10	-	-	0.16	-	0.10
AWD	1.02	0.57	27.76	0.52	67.37	-	1.18	0.10	-	0.15	-	-	1.17	-

Since same manufacturing processes of steel and aluminum are performed globally, chemical composition of the four waste samples are in general compatible with what were reported in the literature, [7, 11, 12, 13] (principally stable metal oxides). The slight deviations are attributed to the metallurgical practices and the variety in alloying elements. This means that most of the metallurgic industry waste produce globally could be used as high-temperature TES material (except the ones rich in Carbon dust like APS).

4.2. *Thermal Stability*

Fig. 3 represents the sample mass percentage as a function of time. During this experiment, the material is subjected to a temperature program from 40 °C to 1100 °C under nitrogen. All mass changes occurred in the first thermal cycle and the mass is almost stabilized in the second heating cycle. Oxidation of metals results in mass gain in the first thermal cycle of EAF slag sample at about 1000 °C. Then almost no significant mass change is observed up to 1100 °C. LF slag experienced a sharp mass loss due to carbon dust decomposition as revealed by FTIR spectrum (vibration mode of carbon dioxide). This is followed by a mass gain of about 2 %, where the mass appears almost to stabilize. Additionally, FTIR spectrum showed that carbon decomposition started to occur in APS at the end of the first thermal cycle. The mass loss is about 55 % of the initial mass. The mass is then stable during the rest of the experiment. On the contrary, AWD shows a mass gain around 200 °C in the first cycle, again due to oxidation of metals such as aluminum and iron. AWD mass stabilized afterward at high temperatures (900 °C to 1100 °C).

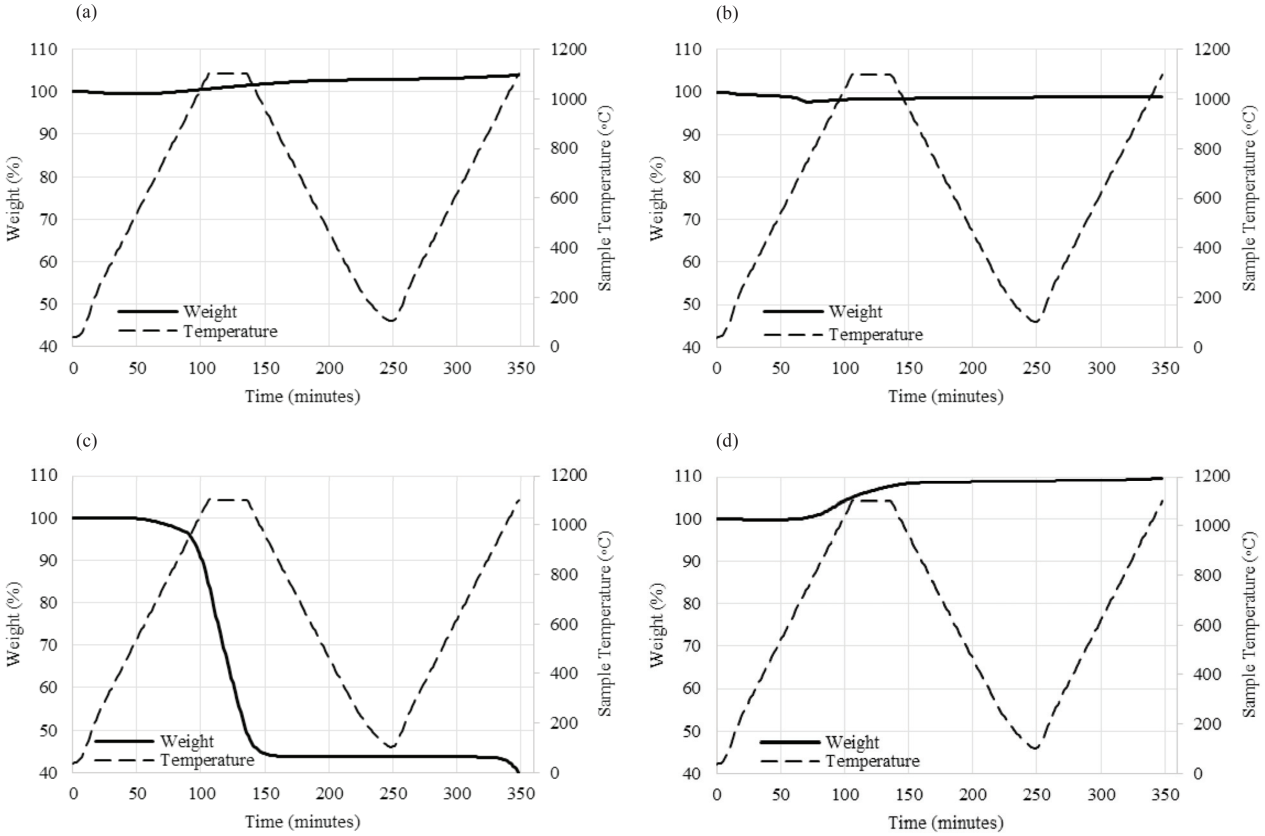

Fig. 3. TGA curves of (a) EAF slag; (b) LF slag; (c) APS; (d) AWD as-received samples

5. Conclusion

Different industrial waste from steel and aluminum industries in the UAE have been identified to be recycled as TES media for high temperature CSP applications. The materials studied in this paper are inexpensive and available in large quantity. Chemical analysis revealed no hazardous contents in EAF slag, LF slag, APS and AWD. A relatively high amount of free iron and aluminum metal have been found in AEF slag and AWD, respectively. Since APS is essentially carbon, this sample is degrading at high temperature and is not suitable for high-temperature storage applications. In general, EAF slag, LF slag and AWD are thermally stable up to 1100 ◦C with slight mass changes at the first thermal cycle. Further thermal characterization to measure heat capacity and thermal conductivity are under way. Additionally, there are attempts to characterize the waste generated from processing AWD, known as aluminum black dross.

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Biography

Dr. Nicolas obtained his Ph.D. in Engineering Science in 2010 at the PROMES CNRS Laboratory in south of France. He worked on thermal energy storage at the National Renewable Energy Laboratory (NREL) in the USA in 2011 then at the CIC Energigune Energy Cooperative Research Centre in Spain in 2012. In 2013, he joined Masdar Institute of Science and Technology in the United Arab Emirates as an Assistant Professor. He is leading the Thermal Energy storage Research Group and chairing the Masdar Institute Solar Platform committee.