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CATALYTIC APPLICATIONS OF LARGE SCALE METAL PROCESSING WASTES

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Introduction

The application of large scale wastes as catalytic resources is an area of active interest.¹ Table 1 summarises the large scale metal processing wastes which will be highlighted in this manuscript and provides an indication of the scale of their production. It can be seen that large volumes of material are produced and whilst in some instances further application to a relatively high degree is well established (e.g. 90 % of blast furnace steel slag is utilised in Germany and ca. 87 % of the slag from the EU is used for building applications²) in others the storage of large volumes of potentially hazardous waste poses a problem (e.g. red mud, the hazardous nature of which is apparent from the tragic events in Hungary in October 2010). Large volumes of waste offer potentially very cheap sources of catalytic materials and in some cases, e.g. red mud, this could provide a component to the solution of a potentially hazardous storage issue in addition to contributing to greater sustainability through the greater degree of utilisation of a wasted resource. As will be outlined below, the wastes themselves may be directly applied as catalysts or they may be further processed so that desired components are selectively extracted and/or their catalytic properties are enhanced. In the former situation, inevitable compromise must be reached between the deleterious potential effects upon selectivity and/or activity of the application of heterogeneous mixtures which possibly have a degree of variation dependent upon source and/or time of acquisition, and low cost. In the summary which follows, examples of both direct application of waste and its pre-treatment to extract catalytically active components will be provided.

Table 1: Reported Production Rates of Various Metal Processing Wastes.

Waste Material	Reported production rate	Reference
Red mud	120 million tonnes per annum	[3]
Slag	249-290 million tons in 2008	[4]
Aluminium dross	5 million tonnes per annum	[5]

Slag

As stated in the introduction, the utilisation of slag is well established, particularly for construction applications. The composition of selected blast furnace slags from different sources is presented in Table 2.

Table 2: Composition of Selected Blast Furnace Slags (wt.%) (a more complete list and fuller analyses are given in the study of Hargreaves *et al.*²)

Origin	CaO	SiO ₂	Al ₂ O ₃	MgO	Reference
Turkey	36.80	36.00	14.84	7.10	[6]
China	41.78	40.55	7.60	6.16	[7]
Iran	37.20	36.20	8.00	10.30	[8]
Japan	42.99	33.52	13.77	6.28	[9]
Taiwan	41.67	43.39	14.47	6.49	[10]
Egypt	29.83	41.46	11.36	1.35	[11]

Upon inspection of the table, it can be seen that CaO, SiO₂ and Al₂O₃ are significant components. Similarly to the situation with fly ash, it is the latter two components which have dominated the application of slag to make zeolites which could be of catalytic relevance. In such instances, the presence of >15 wt.% CaO can be problematic due to inhibition of zeolite nucleation as a consequence of calcium silicate formation.¹²

Accordingly, strategies to alleviate this problem have been devised as summarised in the schematic presented in Figure 1. In this figure, it can be seen that hydroxyapatite-zeolite composites and hydrotalcite and zeolites can be formed. Of particular relevance to heterogeneous catalysis is the ability to prepare Faujasite type zeolites (X and Y) which can be of potential interest for large scale acid catalysed petrochemical applications, such as fluidised catalytic cracking.¹³ In contrast, hydrotalcites represent interesting base catalysts and/or precursors to mixed metal oxides.¹⁴ In terms of this class of material, the preparation of hydrocalumite from slag and its modification has been recently reported^{15,16}. Such materials have been applied to a wide range of base catalysed reactions including Knoevenagel condensation,¹⁵ transesterification,^{15,16} cycloaddition of epoxides with CO₂¹⁵ and oxidation of alkylaromatics with O₂.¹⁵ In the case of transesterification, a process of major contemporary interest in terms of biofuel production, interfusion of Fe and Mn slag derived impurity elements into the hydrocalumite promotes catalytic activity.¹⁶ Figure 2 presents a schematic summarising the preparation of the various hydrocalumite related phases and Figure 3 a summary of the behaviour of some for transesterification. Performance was observed to be a very strong function of

calcination temperature with the more active catalysts comprising CaO-MgO-mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$) ternary phases. In the case of slag derived ternary phase analogues impurity Fe and Mn elements were proposed to lead to enhanced retention of Cl^- on the surfaces of the CaO and MgO phases providing protection upon storage in air.

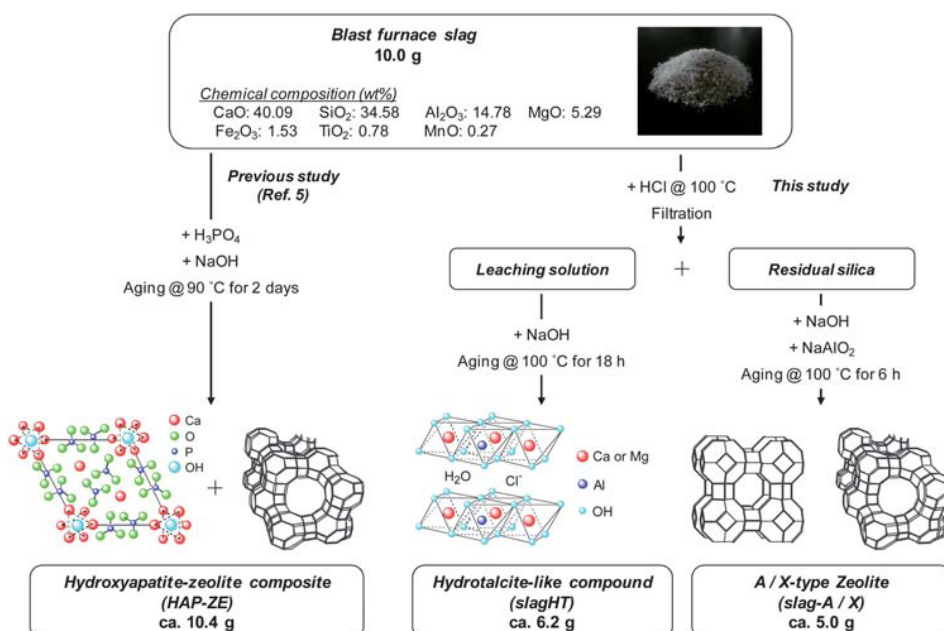


Figure 1: Summary of the conversion routes for slag containing > 15 wt.% CaO, reproduced from the study of Kuwahara *et al.*⁴ with kind permission from the Royal Society of Chemistry. Within the schematic “This study” refers to the study of Kuwahara *et al.*⁴ and “Previous study (ref.5)” refers to the study of Cheng and Chiu.¹⁰

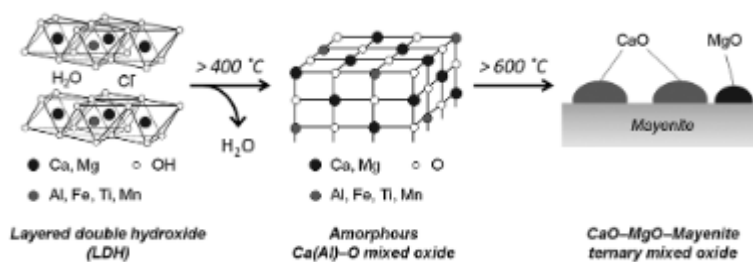


Figure 2: Conversion processes related to hydrocalumite generated from slag. Reproduced from the study of Kuwahara *et al.*¹⁶ with kind permission from the Royal Society of Chemistry.

Slag has also been utilised in the preparation of solid base catalysts for the preparation of diethylcarbonate from ethyl carbamate and ethanol.¹⁷ Dissolution of the slag with HCl was enacted to form a solution containing most of the elements from the slag followed by precipitation with NaOH and calcination in air. By such means, active catalysts of higher surface area comprising reduced levels of silica could be obtained.

The application of steel slag waste modified with manganese to form catalytic particle electrodes for the degradation of rhodamine has also been recently documented.¹⁸

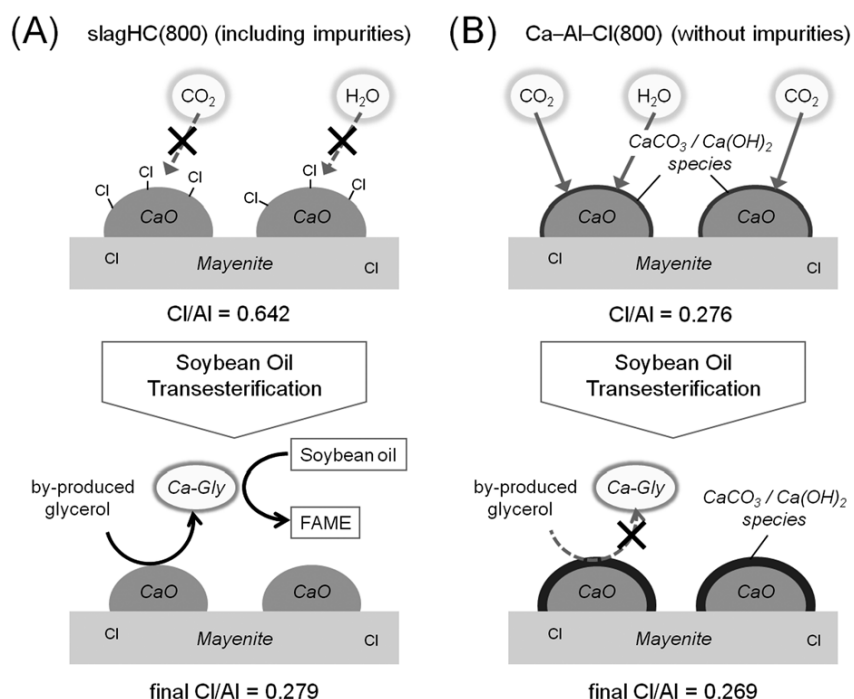


Figure 3: Summary of transesterification performances of a model hydrocalumite derived material and that of an analogue prepared from slag. Figure reproduced from the study of Kuwahare *et al.*¹⁶ with kind permission from the Royal Society of Chemistry.

Aluminium Dross

Aluminium dross is a by-product of aluminium production and recycling. It is subdivided into white dross and black dross and is formed upon reaction of molten aluminium with air generating surface oxide and nitride phases. White dross is ca. 80 wt.% Al and is formed during the Hall-Heroult Process whereas black dross, which

is typically 5-20 wt.% Al, is formed in aluminium recycling and also secondary processing of white dross. Whilst some dross is applied as a deoxidiser in the production of steel, most of the waste material is landfilled. Table 3 presents an indication of the composition of dross.

Table 3: Metal Components of Aluminium Dross.¹⁹

Al	Mg	Si	Pb	Zn	Ca	Na	K	Fe	Ti	Mn
89.1	3.8	0.2	0.2	0.7	1.3	0.7	0.8	2.5	<<0.1	0.6

The dross detailed in this table has been used to generate ALPO-5, a zeotype material of potential interest for shape elective catalysis.¹⁹ This material, albeit impure, has been prepared by treating the dross with phosphoric acid and applying triethylamine as a structure-directing agent. Al(OH)₃ in conjunction with Al extracted from dross has been applied to the preparation of pure ALPO-5 has been detailed in the literature as has its Cr containing counterpart, CrAPO-5.²⁰ The application of the latter material as a catalyst for the production of tetralone from the oxidation of tetralin with t-butylhydroperoxide has been detailed. In terms of enhanced porosity, hexagonal mesoporous aluminophosphates and their chromium containing derivatives have also been prepared using dross by application of a different templating procedure.²¹

As can be anticipated, dross can also be applied as a source of catalytically active alumina. In this instance, H₂SO₄ leaching of dross and subsequent treatment with aqueous ammonia can be applied to yield aluminium hydroxide which can be subject to further calcination to generate transitional aluminas.²² The alumina recovery can be enhanced by washing the dross. In the case of the AlPO phases, impurities can also influence the crystallite sizes reportedly being found as a result of seeding.²⁰

Red Mud

Red mud, or bauxite residue material, is arguably the most infamous large scale waste following the tragic event in Kolontar, Hungary in October 2010.²³ It is a large scale by-product of the Bayer Process in which aluminium is extracted from bauxite via reaction with hot concentrated caustic soda. It is a highly alkaline material which presents disposal problems, being largely lagooned. Its composition is dominated by its iron content, from where its distinctive colour originates, and is reflective of the bauxite from which it is derived. It therefore has a geographical variation as illustrated in Table 4 which, as is conventional, assumes metals to be present in the

form of their binary oxides. This is, of course, a simplification and it is possible to define a mineralogical composition as presented in Table 5.

In addition to being geographically variable, the composition from a single lagooning site can also change with time, reflecting changes to the composition of the bauxite source used in the processing. These considerations have significant impact in those instances where red mud is applied directly as a catalyst. This aspect is exemplified in Figure 4 where three different sources of red mud have been directly applied as (pre-)catalysts for methane cracking – two of these samples were sourced from the same location but with a two year interval (RM4 and RM7) whereas RM6 was obtained from somewhere else. Differences in both the powder XRD patterns of the materials are evident (Figure 5) as well as the differences in the mass normalised hydrogen formation rate profiles presented in Figure 4.

Table 4: Chemical Composition of Different Red Mud Samples.²⁴

	Weipa (Australia)	Trombetas (Brazil)	South Manchester (Jamaica)	Darling Range (Australia)	Iszka (Hungary)	Parnasse (Greece)
Digestion temperature (°C)	240	143	245	143	240	260
Components (wt.%)						
Al ₂ O ₃	17.2	13.0	10.7	14.9	14.4	13.0
SiO ₂	15.0	12.9	3.0	42.6	12.5	12.0
Fe ₂ O ₃	36.0	52.1	61.9	28.0	38.0	41.0
TiO ₂	12.0	4.2	8.1	2.0	5.5	6.2
Na ₂ O	9.0	9.0	2.3	1.2	7.5	7.5
CaO	-	1.4	2.8	2.4	7.6	10.9
Others	3.5	1.0	2.8	2.4	4.9	2.3
Loss on ignition	7.3	6.4	8.4	6.5	9.6	7.1

Pre-treatment procedures can be undertaken which may, in addition to enhancing the catalytic properties of red muds, also mitigate variation in their performance. Perhaps the most well - established of these is that detailed by Pratt and Christoverson.²⁶ In this procedure, initial acid dissolution of red mud is followed by subsequent base precipitation.

Studies into the application of red mud as a catalytic material or as a catalyst precursor are reasonably well established. A comprehensive review of this area has been published by Sushil and Batra.²⁷ In more recent years, predominant emphasis has been placed upon the application of red mud as a catalyst in relation to renewable fuel applications. Amongst these, red mud has been applied to the thermal decomposition of acetic and formic acids – compounds stated to be of relevance for the upgrading of pyrolysis bio-oil.²⁸ In this study, formic acid was proposed to act as an internal source of hydrogen through the formation of synthesis gas and the water gas shift reaction. Higher hydrocarbons as well as CO₂ were formed and the red mud was converted to a non-alkaline mixture of Fe₃O₄ and Fe. In a related study, acetic acid and formic acid were applied to generate reduced red mud which was used to upgrade hemp seed pyrolysis bio-oil when hydrogen was supplied as an external reductant.²⁹ It was suggested that the reduced red mud could find application as an iron ore or a component of aluminoferrite belite cement.

Such an approach was also proposed in a related study for upgrading of a pyrolysis bio-oil derived from hardwood.³⁰ Optimisation of the neutralisation of red mud by pyrolysis bio-oil applying a statistical design of experiments approach has recently been reported with the aim of providing a starting point for scale-up and the remediation of red mud lagoons using a renewable biomass derived resource.³¹

Co-generation of a low-grade fuel and a value added derivative of red mud have been reported in a study which upgraded the crude untreated waste stream from biodiesel.³² This stream comprised glycerol, methanol, water and free fatty acids and was considered a very low cost “reagent” for the upgrading of red mud into a less hazardous and a value-added material whilst approximately doubling the heat value of the waste stream.

Table 5: Mineralogical Composition of Various Red Mud Samples.²⁴

Components (%)	Weipa	Trombetas	South Manchester	Darling Range	Iszka	Parnasse
Gibbsite	33.0	-	33.0	5.6	-	-
Haematite	3.5	38.0	3.5	14.5	33.0	38.0
Goethite	18.0	19.0	10.0	14.5	6.0	1.0
Sodium aluminium hydrosilicates	27.0	27.0	27.0	5.4	32.0	26.0
Illite	2.0	-	-	4.7	-	-
Boehmite	2.0	0.6	2.0	3.5	0.8	0.6
Diaspore	-	1.2	2.0	2.5	0.7	0.6
Ca-Al silicate	-	-	-	1.7	12.5	10.0
Calcium titanate	-	1.5	-	-	7.0	10.5
Calcite	0.5	1.4	-	2.3	3.0	3.6
Quartz	6.0	2.2	0.5	37.1	-	-
Anatase	2.0	2.5	6.0	1.0	-	-
Rutile	6.0	0.8	2.0	-	-	-
Sodium titanates	-	-	6.0	0.6	-	-
Magnetite	-	-	-	1.3	-	-
Chamosite	-	-	-	-	-	6.0
Ilmenite	-	-	-	1.0	-	-
Others	-	5.8	-	3.4	5.0	3.7

Whilst the application of red mud for SO₂ scrubbing was established by Sumitomo a number of years ago,³³ more recent studies has also focussed upon its application to removal of sulfur from feedstreams by various routes. By using a combination of red mud, acetic acid and H₂O₂, the desulfurisation of a simulated diesel containing dibenzothiophene has been accomplished.³⁴ The resultant dibenzothiophenes sulfoxide and sulfone were then reversibly trapped on the red mud surface. The process is outlined in Figure 6. Regeneration of the red mud by thermal means could then be accomplished.

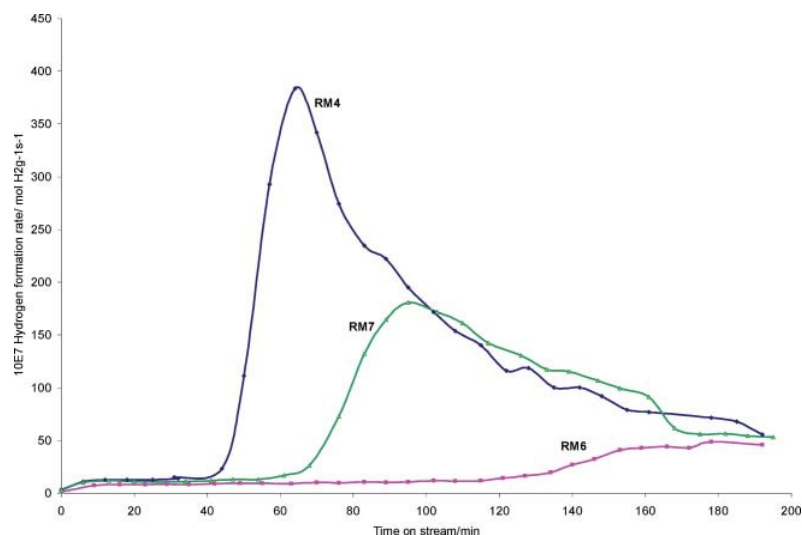


Figure 4: Mass normalised hydrogen formation rates with time on line from three red mud samples applied to methane cracking at 800 °C. Figure reproduced from the study of Balakrishnan *et al.*²⁵ with kind permission from the Royal Society of Chemistry.

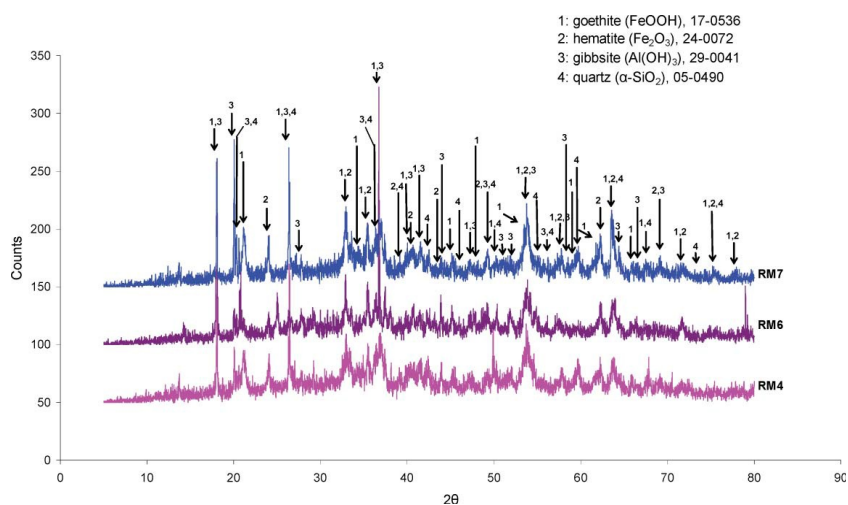


Figure 5: Powder x-ray diffraction patterns (Cu K α radiation) for red mud samples tested in Figure 4. Figure reproduced from the study of Balakrishnan *et al.*²⁵ with kind permission from the Royal Society of Chemistry.

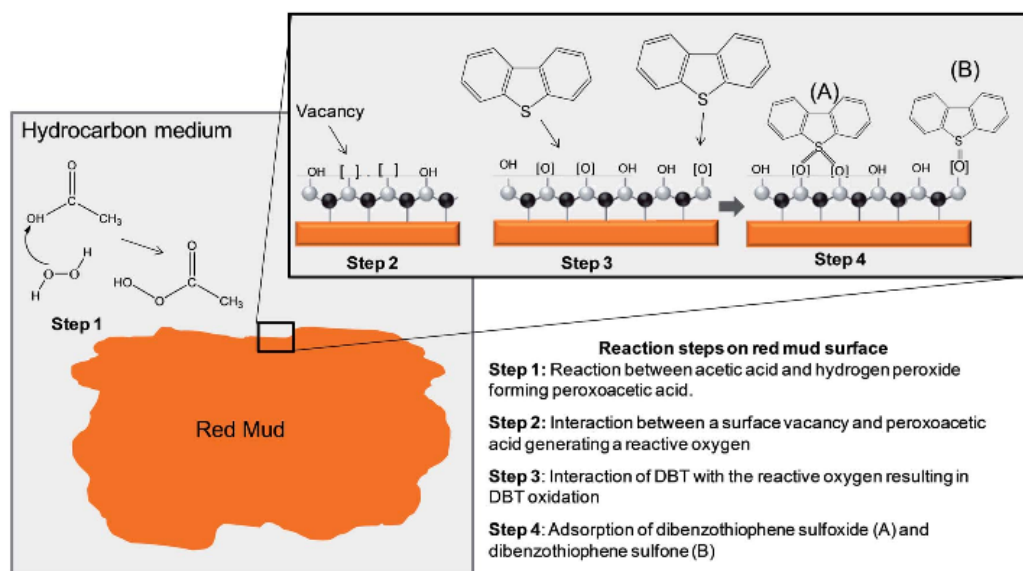


Figure 6: Steps in the desulfurisation of a model diesel stream as outlined in the study of de Resende *et al.*³⁴. Figure reproduced from the study of de Resende *et al.*³⁴ with kind permission from the Royal Society of Chemistry.

Gold doped modified red muds have also been documented for H_2O_2 based desulfurisation with carbon coating being demonstrated to yield advantages in bi-phasic systems due to amphiphilicity³⁵.

Phosphoric acid modified red mud has been identified as an active disposable catalyst for slurry phase hydrocracking of vacuum residue oil³⁶. In this instance, the influence of the acid treatment was proposed to be the reduction of particle size of the red mud, facilitating the active sulfide form.

A very interesting approach to the transportation of associated petroleum gas resulting from off-shore platforms has been recently outlined³⁷. In this approach the petroleum gas is converted into carbon upon red mud generating an easily transportable species which can be subsequently treated in a remote second step using H_2O to liberate syn gas, with the regenerated iron oxide being further applied to a second cycle and, so on.

Conclusion

In this overview, a brief description of some of the recent studies related to the application of three large scale metal processing wastes to the area of heterogeneous catalysis has been outlined. In many instances, the application of

such wastes provides a low cost option for the preparation of catalysts which are, consequently, disposable. Particularly in the case of red mud, this can provide a component to the solution of problems associated with the storage of large volumes of an undesirable waste, since the resultant form of the material is generally less hazardous and/or of higher value. Upon surveying the academic literature, it is clear that the application of wastes as resources for catalysis is an area which is becoming increasingly well recognised and investigated.

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