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Recovery of values from spent high temperature shift catalysts of urea fertilizer factory

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ABSTRACT

Spent high temperature shift (HTS) catalyst of urea fertilizer factory containing 59% iron and 6% chromium has been roasted with sodium carbonate. Iron contained in the catalyst was converted to iron oxide and chromium to sodium chromate. The conditions for the formation of brown and black iron oxides have been established. The possibilities to produce lead chromate from sodium chromate have also been examined. The composition and the structure of the iron oxide pigment produced compares well with the iron oxide pigment available commercially. The results obtained suggest that an acceptable technical, commercial and environment friendly solution to the disposal the spent high temperature shift catalysts through recovery of values contained in it is available.

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KEYWORDS

Urea fertilizer plants;
High temperature shift
catalysts;
Recovery of values.

INTRODUCTION

Since the ammonia technology started spreading, Fe and Cr has been considered as the most suitable high temperature shift (HTS) catalyst working in between 360 to 430°C. In general, the working life of the HTS catalyst is about five years; and a full charge has to be replaced in the reactor after this time interval. The major fertilizer plants of Bangladesh use about 350m³ of HTS catalyst weighing about 400 metric tons. These catalysts are, in general, replaced after a 5 years period and thus about 80 metric tons of spent catalysts are discarded each year.

Historically spent catalysts have been disposed off as land-fill. In the land fills the metals present in the catalyst can get leached by water and pollute the environment. Disposal of spent catalyst materials, which con-

tains appreciable amounts of heavy metals, is thus environmentally hazardous. In recent years environmental laws concerning spent catalyst disposal have become increasingly more stringent. As a consequence, efforts are being made to develop processes for the regeneration of the spent catalyst and also for the treatment of the spent catalysts to reduce leachability. These treatment methods are however, highly energy intensive and very expensive.

These catalysts contain appreciable amounts of metal values and can be treated as potential sources of metals. Increasing concern for the preservation of natural resources of metals has focused attention to the secondary sources and considerable progress have been made towards the recovery of metal values from various secondary sources that include spent catalysts. Extraction of metals from such secondary sources re-

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quires less energy, helps preserve natural resources and reduces environmental pollution caused by production from primary sources (ores). Spent HTS catalysts contain significant quantities of iron and chromium. Thus the development of a method for the recovery of values from spent HTS catalyst is important from both economic and environmental points of view.

Reports on research efforts that have gone into recovery and recycling of critical metal values from the spent catalysts^[1-4] generally discuss leaching of the spent catalysts with acidic or alkaline solutions. Most procedures emphasize recovery of metals like Mo, V, Ni and W. In many cases the extraction of metal values is poor and only limited attempts have been to recover/recycle all of the metals from the spent catalysts with a single extractant.

Utilisation of spent catalyst as raw materials for the production of other valuable products is an attractive option from environmental as well as economical points of view. This paper presents the results of investigation aimed at the development of an acid free and economic route for the processing of spent high temperature shift catalysts (SK 201) of urea fertilizer factories. The major metallic element in the catalyst under consideration is iron, a bulk commercial metal. The other important metal is chromium but the content is very low to warrant extraction of metallic chromium. In view of the availability of a small volume of source material within Bangladesh (about 80 tons/year) the recovery of the values in the form of elemental iron or an alloy of iron and chromium was not considered an attractive option.

A theoretical investigation showed that sodium carbonate could oxidise iron to iron oxide. Addition of sodium carbonate to a mixture of iron and chromium could also lead to simultaneous formation of sodium chromate. Both iron oxide and sodium chromate have wide applications as pigment. Iron oxide pigments are the second most important pigment after titanium dioxide. They are non-toxic, relatively inert, weather resistant and mainly opaque. Red iron oxide pigments are used for making paints and inks. Other important uses include burnishing of wooden furniture, colouring of paper, plastic and crayons. In the construction industry iron oxide pigments are used in ready mixed concrete, concrete products, roofing tiles, pavers and paint. Non-metallurgical applications of iron oxides include dense

medium separation.

Sodium chromate is used in the industry as an important source for manufacture of chromium compounds. It is used in certain types of corrosion control applications such as coolants containing alcohols and water cooling systems by forming a protective film on metal surfaces. Other applications include pigment formulation, mordant for dyeing wool, wood preservative, oil well drilling fluids and catalysts.

Attempts were, therefore, concentrated towards the utilization of the spent catalyst as raw material for the production of iron oxide and sodium chromate for possible use as pigment and generate as little final waste as possible in the process.

MATERIALS AND METHODS

Material

Copper promoted iron/chromium based high temperature shift catalyst (SK 201) used in this investigation was supplied by KAFCO (Karnafully Fertilizer Company) Limited, Chittagong, Bangladesh. Chemical characteristics of the catalyst SK 201 is given in TABLE 1. The other characteristics were: Average bulk density, gm/ml: 1.23, crushing strength, Kg: 1.625 Kg and size: 6mm x 6mm (1/4 x 1/4 inch). The other major raw material was soda ash (Na_2CO_3) of commercial grade. Soda ash is easily available, easy to handle and the cost is acceptable.

TABLE 1 : Chemical characteristics of the catalyst SK 201

Element	Weight percent
Fe	59
Chromium	6
Graphite	4
Sulphur	< 150 ppm
Balance	Oxygen as metallic oxides
Copper promoted	

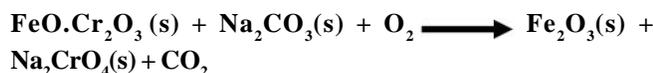
All chemicals and reagents used in the study were of commercial grade.

Method

The samples of spent high temperature shift catalyst were ground in an agate mortar to a size to pass a 140 mesh screen. 15 gm of the powdered catalyst was intimately mixed with 10 gm of sodium carbonate (Na_2CO_3)

and roasted in an electric muffle furnace in the temperature range of 600 – 900°C for periods of up to 3 hours. A controlled flow of air was directed towards the mixture during roasting to assist the process of oxidation. The major focus of the investigations was on the determination of optimum conditions for the production of red iron oxide and sodium chromate and on the effective and economic separation of the two products.

The reactions involved can be summarized as:

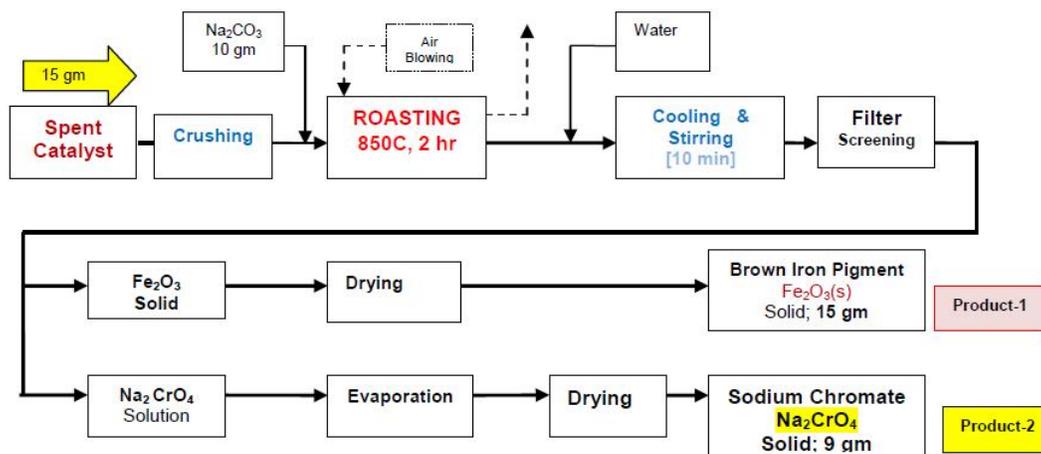


X-ray diffraction techniques were used to characterize the products (iron oxide) obtained.

RESULTS AND DISCUSSION

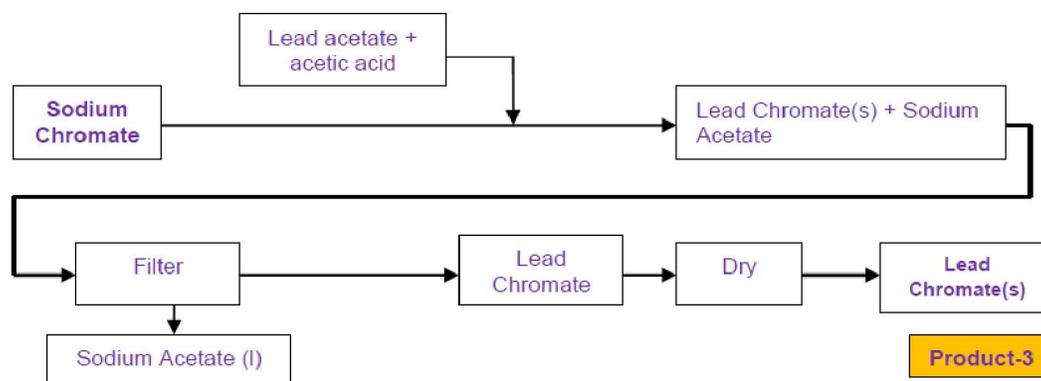
The details of the processes used for the production of iron oxide and sodium chromate are shown as Flow-sheet 1. It may be mentioned that no residues were left and at the same time all the values contained in the spent catalyst could be recovered. Water used for the process could be recycled.

The qualitative tests performed on the samples of iron oxide and sodium chromate in a paint manufacturing factory indicated satisfactory results. However, it was gathered that the paint manufacturers, because of the superior properties of lead chromate, were more interested in lead chromate for the manufacture of yellow paints. Consequently attempts were made to convert sodium chromate to lead chromate and the processing parameters were optimised.



Note: Roasting at a temperature of 950°C would give black iron oxide

Flow sheet 1 : Processing of iron catalyst ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$) to iron oxide



Flow sheet 2 : Processing of iron catalyst ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$) to Sodium chromate

The processes involved in the conversion of sodium chromate to lead chromate and sodium acetate is shown in Flow sheet 2.

$\text{Na}_2\text{CrO}_4 + (\text{CH}_3\text{COO})_2\text{Pb} \longrightarrow \text{PbCrO}_4 + \text{CH}_3\text{COONa}$
Sodium chromate can also be converted to sodium or potassium dichromate. The reaction involving sodium

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dichromate is shown below:



However, this possibility was not explored further.

X-ray diffraction patterns (Figure 1) recorded on iron oxide produced showed that the pattern is identical with that of standard Fe_2O_3 .

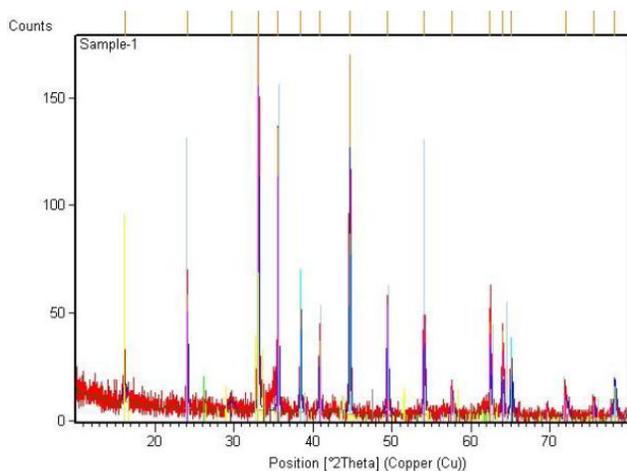


Figure 1 : X-ray diffraction patterns recorded on iron oxide (Fe_2O_3) produced

CONCLUSIONS

The important features of this investigation can be summarised as follows:

- a) It is possible to produce a brown or a black iron oxide pigment and sodium and lead chromate reagents (chemicals) through an acid free process using very simple equipment. All these reagents have wide industrial applications.

- b) All the components of the spent catalyst could be transformed into useful value added product. This could be an environmentally acceptable process for the disposal of spent high temperature shift catalyst of urea-fertilizer factories.

ACKNOWLEDGEMENT

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