VALORISATION OF ALL MATERIALS RESULTED FROM THE COMPLETE PROCESSING OF SPENT CATALYSTS BASED ON COPPER TETRACHLOROALUMINATE DISSOLVED IN ALKYL BENZENE SOLVENT TYPE

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Abstract

This paper deals with an advanced procedure and plant for the recovery of useful products (toluene and metallic copper) from organic catalyst hazardous waste, based on copper tetrachloroaluminate dissolved in an alkyl benzene type of solvent, used for the selective separation of carbon monoxide resulted during hydrocarbon combustion. At the same time, a new inorganic composite coagulant made of a mixture of iron chloride and aluminium chloride is obtained. The procedure is the object of a patent application and solves both the problems of decontamination for a very hazardous waste type and the recovery of each component of the organic complex under exploitable forms.

Keywords: *alkyl benzene, composite for coagulation, metallic copper, toluene*

The technology of carbon monoxide selective separation by complexation/decomplexation of carbon monoxide in an organic solvent containing cuprous aluminium chloride ($CuAlCl_4$) was initially developed and commercialised by the American company Tenneco in 1976. Since 1983, the KTI trust in Minnesota has been the exclusive owner of the patent, licence and technology. At present, there are ten units ranging from 270 to 5500 NM^3/Hr of recovered CO and operating in hydrocarbon processing units [1].

In the technological process of carbon monoxide selective separation, the flue gas is bubbled through the liquid flow containing the complex catalyst. The CO specific reaction follows, thereby isolating CO from the other compounds resulted from the partial oxidation of methane or other hydrocarbons. When CO is separated by this method, over 99% of the CO contained in the gas flow can be recovered [2].

This method was later employed as an application in the selective separation of olefins, alkynes or certain aromatic compounds, using the same catalyst and technology [3-7]. In any of these applications, the catalyst is a bimetallic complex of the following type:

$$\mathbf{M_IM_{II}X_n{*}ALB} \qquad (1)$$

where:

- M_I – group IB metal, most frequently Cu(I);
- M_{II} - Al(III);
- X - halogen ion, usually Cl^-;
- ALB – alkyl benzene derivative, usually toluene.
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The catalyst can undergo complexation/decomplexation cycles for a long time. However, in time the accumulation of alkylation by-products and sulphur-containing organic derivatives or polymerisation causes catalyst poisoning. Due to the large amount of metals and the organic solvent, the spent catalyst becomes a hazardous type of waste that can be neither eliminated through established processes nor stored in treatment pits, because it causes increased pollution. Moreover, through the hydrolysis of the complex chloride on contact with the air, the spent catalyst releases hydrogen chloride which harms the environment, corrodes metals and is also highly toxic for men and animals.

In view of the above facts, the authors of this paper have applied for a patent on the method of NOx removal from spent catalyst waste of the mentioned type. The economic result of NOx removal is the simultaneous recovery of the organic solvent that becomes pure enough to be reintroduced in the industrial circuit, the IB-group metal as an element with 95% purity, and aluminium as a dicomponent coagulant that can be used in wastewater treatment.

Up to now, several methods of copper and toluene recovery from spent catalyst waste have been identified worldwide:

a) Method I – Tenneco Chemicals [8] suggested copper separation by treating the spent catalyst with anhydrous ammonia; cuprous chloride as precipitate and NH_3AlCl_3 in toluene are obtained. The use of anhydrous ammonia at -25ºC made this method both unfeasible and inefficient.

b) Method II. The second Tenneco Chemicals method (patented in 1976) [9] was based on treating the spent catalyst with 10% aqueous ammonium chloride solution. The resulting $[Cu(NH_3)]^{2+}$ complex was treated with aluminium and reduced to copper metal. The low efficiency and the aluminium loss through overflowing proved this method economically and ecologically inefficient. The method was never applied in industry.

c) Method III of Tenneco Chemicals (patented in 1979) [10] suggested the neutralisation of the spent catalyst with an alkaline solution, namely the hydroxide of an alkaline metal with a pH of 6-7. Copper oxide and aluminium hydroxide were formed. The organic and inorganic phases were separated. The former was incinerated, while the latter was treated with sodium hydrosulphide (NaHS) aqueous solution. The resulting Cu_xS_y type sludge was discarded in a waste pond. The method is uneconomical because the metals contained in the spent catalyst are not recovered at all and it causes environmental pollution.

d) Method IV of Tenneco Chemicals [11] was based on a much more effective copper recovery process, namely treating the spent catalyst with diluted HCl or water for the separation of the organic and inorganic phases. The organic phase was incinerated, the inorganic was treated with aluminium, resulting powdered copper. The aqueous phase that resulted after copper separation was treated with NaOH and the resulting aluminium hydroxide was discharged in the sewer. The method is unproductive because the copper recovery rate is low, the other useful materials in the spent catalyst are not re-used and the environment is polluted with large amounts of aluminium ions.

e) Method I of Dow Chemical Company (patented in 1981) [12] is based on a copper recovery process with better copper separation results. It involves treating the organic catalyst with water to form cuprous halide, the separation of the aqueous and organic phases and the oxidation of cuprous halide to cupric halide which is more suitable to contacting with metals higher than copper in the electromotive series, like aluminium, and the separation of copper metal from the aqueous mixture that contains aluminium chloride.

f) A variant of the Dow Chemical method is based on treating catalyst waste with 1-6 molar hydrochloric acid, thereby eliminating the oxidation of Cu^+ to Cu^{2+}. The other stages remain unchanged.

g) A possible method of treating the aluminium oxychloride resulting from contacting the complex catalyst with water [13] after copper separation is to immobilize it in Portland cement bentonite clay matrices, under the form of a non-conventional building material.

h) Internally, the issue of this kind of spent catalysts was approached in a research contract between the authors and Dolj Chim Craiova [14]. This deals only with the ecological neutralisation of the organic solvent and metal ions under the form of salts which are said to be important. It reproduces fragments of the methods given in the above a)-f) paragraphs. The implementation stage of the research results is not known, but the approach does not bring any change in the valorisation of aluminium or toluene.

All cases are based on the neutralisation of the components for discharge purposes [11-12], but none of them reports any technology that facilitates aluminium valorisation [10-14].

In 1981, Dow Chemical Company [12] improved the copper recovery method by increasing the efficiency of the metal separation. However, no results of studies regarding aluminium and/or toluene valorisation were reported.

The above short presentation clearly reveals that none of the catalyst waste treatment methods based on cuprous aluminium tetrachloride dissolved in toluene solves the problem of NOx removal or that of the advanced recovery of useful products simultaneously with the quasi-total reduction of waste that requires disposal or storage through special resource-consuming processes. Consequently, the common major drawbacks of all reported methods are the following:

- the partial recovery of a single useful product (toluene or copper), the other components remaining under the form of waste specific to each recovery technology;
- the generation of new hazardous waste specific to each partial recovery technology;
- aluminium chloride (about 70% of the total catalyst amount) is found completely as waste solutions of concentrations that vary with each case but are equally polluting and corrosive, their only destination is to be stored in special hazardous waste landfill sites;
- the provision of special storage conditions (sealing of $AlCl_3$ containers to avoid hydrolysis in contact with air humidity and their regular changing because of increased corrosion through the embrittlement of the storage container materials), which generates additional expenses long time after the catalyst lifecycle has ended.

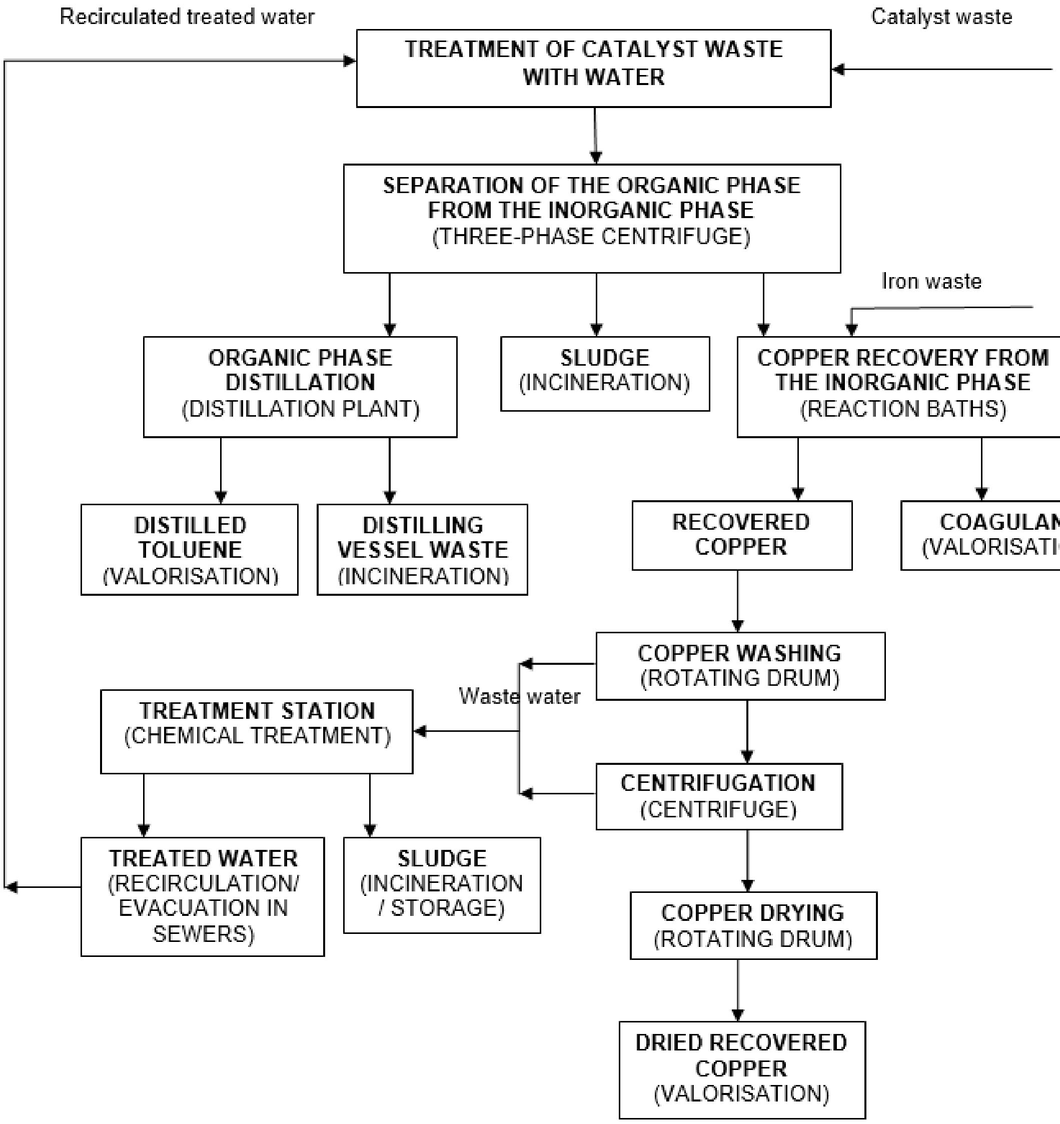

Figure 1. Flow chart for the process of treating $M_IM_{II}X_n$*ALB-type spent catalyst waste

Compared to the other previous methods of treating toxic spent catalyst waste, **the method of total recycling and valorisation of all its components** (**the flow chart** shown in figure 1) includes the following stages [15]:

1. separation of organic and aqueous phases by hydrolysis;
2. obtaining 99% purity toluene (entirely reusable in organic syntheses or solvent production) by double distillation;
3. copper recovery as metal powder through the carburising reaction of the aqueous phase, using sheet metal waste from the incineration of packaging containing hazardous substances;
4. complete recovery of the aluminium from the spent catalyst by obtaining a composite coagulation reagent Al (III) – Fe (III); the proposed method eliminates the discharge of aluminium III-containing wastewater.

All the specified processing steps were adjusted in our own laboratory and followed by the technical team of SC PRO AIR CLEAN ECOLOGIC SA Timișoara. The processing of about 130,000 kg of spent catalyst generated 75,000 kg of toluene and 27,000 kg of copper which were separated and recovered for further re-use.

The amount of aluminium- and iron-based coagulation reagent (2.8 g/dm^3 Fe^{2+} and 1.7 g/dm^3 Al^{3+}) that resulted from the carburising of the aqueous phase for metal copper recovery was about 200,000 kg.

The composite coagulant was tested in the laboratory on three different types of wastewater from oil product processing industry, textile industry and printing activities. In all cases, turbidity was reduced with over 85% and the organic content expressed as TOC was reduced with about 70% [15].

The results obtained in the laboratory stage recommended the pilot testing of the product in the sewage treatment plants belonging to water and sewerage companies in several Romanian localities with which our company has signed cooperation conventions.

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