

REDUCTION OF NICKEL LEACHABILITY FROM IGCC SLAG

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KEYWORDS: Nickel, Slag, gasification, leachability

ABSTRACT

In the slag produced in the Puertollano Integrated Gasification Combined Cycle (IGCC) power plant, nickel occurs in the pyrrhotite (Fe-Ni_{1-x}S) framework structure and as Ni-sulphides. The fine particle size of these species accounts for a fast oxidation to Ni-sulphates in water leaching. The high solubility of Ni-sulphates may result in high Ni extractable levels, limiting the potential applications of slag. Preventive methods for producing uniform and slag (low extractable Ni levels) were tested on three slags produced at different operational conditions. Different ammonia, MgO and water solutions were tested as coolant agents in the slag cooling tank at different operational parameters (temperature, solution/slag ratios, residence time and pH). In all cases the Ni concentration in the tank cooling solutions are higher than in the slag tank cooling solutions from current operational conditions, giving rise to low soluble Ni in the slag end-product. Both, a high pyrrhotite and Ni sulphides dissolution and the formation of MgO and NH₄Cl by ammonia solutions results in a slag end-product falling in the inert range for landfilling materials according to the leachable limits established by the 2003/33/EC Decision. In view of these promising results ammonia solutions are now being tested in the Puertollano IGCC slag cooling tank. Furthermore the Ni extraction from slag being incorporated in the slag tank cooling solution and the re-circulation of the solutions may result in an enrichment of this metal. Consequently this slag tank cooling solutions may be a potential source for the recovery of this valuable element.

1. INTRODUCTION

Slag is defined as a grained inorganic material deriving from molten ash in coal combustion/gasification at temperatures of 1500-1700°C, subsequently removed by wet processes. The coarse particle size of slag (commonly 90% >4mm) and the robustness of this coal combustion by-product make them favorable for a number of valuable applications including fine aggregate in asphalt paving; granular base; soil stabilization/waste solidification; component of blasting grit and roofing granules; fill material for structural applications and embankments; raw material in concrete products; snow and ice traction control material and of acoustic barriers[1-4]. In the conventional Pulverised coal combustion plants (PCC) the production of slag accounts for around 20% of the ash, while in entrained flow gasifiers, around 90% of the ash is removed as slag. In this type of gasifier the fuel and the gasification agents flow in the same direction. Fuel is injected dry (with nitrogen) or wet (with water), following pulverisation to <0.1 mm along with the reactant gases by means of partial combustion burners. The temperature (1200-1600 °C) and the velocity of the gasifying agents are much higher when compared with that of fixed and fluidised bed gasifiers. Given the short residence time of the particles it is necessary to operate under slagging conditions to obtain a high carbon conversion.

The 335 MW Puertollano IGCC power plant is the largest IGCC plant worldwide. It is fed with a mixture of a local high volatile bituminous coal rich in metals and semi-metals and pet-coke, supplied by an oil refinery. Limestone is added (2–4%) to the feed fuel blend as a fluxing agent. The gasification is carried out in a pressurized entrained flow gasifier working at 1200-1600°C and 25 bars. In this IGCC power plant two types of slag are produced when this is removed from the bottom of the gasifier and subsequently cooled with water. During this process two density fractions of the bulk slag are segregated by gravity. The low density (close to 1g/cm³) and fine grain size particles remains as a supernatant fraction of the bulk slag (fine slag) while the coarse and high density fraction of the slag (1.8-2.3 g/ cm³) kept in the bottom of the discharge vessel. Since fine slag contains high proportions of C (up to 60 %) it has to be removed from the discharge vessel to avoid over saturation of the cooling water. The annual mean of fine slag production is 5.7 tonnes. This material is re-circulated to the gasifier, and then it cannot be considered as an actual

by-product. The Puertollano IGCC slag (coarse and high density fraction) is mainly made up [5] of an amorphous Al–Si glass (>99%). Anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), clinoferrosilite (FeSiO_3), orthoferrosilite ($(\text{Fe}, \text{Mg}) \text{SiO}_3$) and Al–chromite Fe (Al,Cr) $_2\text{O}_4$) may crystallize from the melt if cooling is slow enough. Traces of troilite (FeS) and pyrrhotite (Fe_{1-x}S) are usually present in both slag and fine slag. A complete composition and characterization of the slag produced are reported elsewhere [5].

The use of pet-coke in the feed fuel mixture accounts for relatively high contents of Ni in the Puertollano IGCC slag. Nickel mainly occurs in the pyrrhotite ($\text{Fe-Ni}_{1-x}\text{S}$) framework structure and as other Ni-sulphides (pentlandite, millerite, etc). The occurrence of Fe-Ni sulphide species is probably the product of the segregation of a sulphide melt from the silicate melt at high gasification temperatures in a similar way in that sulphide and silicate liquids are segregated in magmatic process. As a consequence of this segregation Fe-Ni sulphides are found as very fine crystals included in the Al-Si glassy slag grains. The fine particle size of these species accounts for a fast oxidation to Ni-sulphates in water leaching. The high solubility of Ni-sulphates [6] may give rise to high Ni extractable levels, limiting the potential applications of slag [7].

This study focus on testing remediation (preventive and corrective) methods for reducing the leaching potential of Ni from the Puertollano IGCC slag. The main goal is to produce a non-hazardous / inert material adequate for its use in different applications, such as in mine reclamation.

2. METHODOLOGY

2.1. Slag cooling system

In the Puertollano IGCC plant the molten slag flows through the bottom of the gasifier and fall into a water bath immersion well where fragmented and subsequently falls by gravity (residence time of a few seconds) until the slag collector also flooded with water, which distributes the slag in two discharge lines to the lock hoppers (water flooded also work). In the lock hoppers depressurization is performed and the slag and water passes the slag extractors, where slag is

separated from water. The slag is then carried to a storage stockpile.

Throughout the entire system (the immersion well to slag extractors) the water has a temperature of 45-55 °C, alkaline pH (8-9), and the time total residence 3h. The alkaline pH is that required for the separation of the fine fraction of slag (high C content) from the coarse fraction of the slag and it is reached by addition of NaOH. The water is continuously re-circulated and the amount of fresh (new) water supplied to the system to offset the water loss because of moisture in the slag is 4.4- 4.8 m³/h. The contact time in the immersion well (where most of the injected new water) is about 15 minutes and the volume of water inside is 8.5 m³ (water / slag ratio of 20 L/kg).

For a 100% load, produced 26963 kg/h of slag with a water content of 2,032 kg / h and a load of 75% slag produced is 20,165 kg / h 1372 kg / h of water (design data). For this study we selected a slag sample produced on May 14, 2010 at high load conditions (> 75%) and high content of coke (61%) in the mixture of fuel, representing the slag produced in common operation conditions which in turn are the worst-case scenario for Ni leachability. Table 1 shows the chemical composition and the extractable potential of major and trace elements from slag selected.

2.2. Preventive methods

2.2.1. Ni extraction with ammonia

A number of Ni extraction experiments with 25% ammonia solution on Puertollano IGCC slag at lab scale (simulating the conditions in the slag cooling system of the Puertollano IGCC plant) were carried out. The ammonia extraction tests were based on the high affinity of Ni to form highly soluble amine complexes [8,9] and on the use of ammonia in other processes of the IGCC plant. The main goal of this tests was to determine the dissolution potential and concentration of Ni in the ammonia solution (which simulates the solution used for cooling slag in the Puertollano IGCC slag cooling tank) and that of the resulting slag. The experimental conditions of the tests are summarized in Table 2. The solution was then filtered and analyzed.

Subsequently the EN-12457 leaching test was applied to the dried solid residue (simulating the cooled slag produced in the IGCC plant) with and without previous water washing, to determine the extraction potential of Ni and other elements from

this IGCC residue and establish classification as inert, non-hazardous or hazardous according to the EC/332/2003 Decision for landfilling materials.

2.2.2. Ni extraction with water

Based on the fast oxidation of Ni-rich pyrrhotite (Fe-Ni_{1-x}S) to sulfate and subsequent dissolution (Ni sulfate is highly water soluble, xxx g/L) [6], a number of Ni water extraction tests were carried out in the conditions of the Puertollano IGCC slag cooling tank varying the residence time (extraction time 30-60 min) and pH (7-9). The objective is to determine the effect of increasing residence time and reducing pH on the Ni dissolved in the cooling tank solution and on the resulting slag. The extraction residue (slag) was dried and the leaching test was subsequently applied to determine the leaching potential of Ni and establish waste classification for landfilling according to 2003/33/EC Decision.

Table 2. Experimental conditions of the Ni extraction experiments (simulating extraction in the IGCC slag cooling tank).

Test	1	2	3	4	5	6	7
Extractant (cooling solution)	NH ₃ 25 %	NH ₃ 25 %	NH ₃ 25 %	NH ₃ 25 %	H ₂ O	H ₂ O	H ₂ O
pH	9	9	12	12	9	9	6-7
Temperature (°C)	50	50	50	50	50	50	50
Time (min)	15	30	15	30	30	60	30
Solution/slag (L/Kg)	20	20	20	20	20	20	20
Washing	no	no	yes (20mL/g)	yes (20mL/g)	no	no	no

2.3. Corrective methods

2.3.1. Blending IGCC slag with alkaline materials (PCC fly ash)

As a corrective method for reducing Ni leachability from Puertollano IGCC slag, lime-rich and lime-poor PCC fly ash were selected. The selection of lime-poor PCC fly ash for the experiments is due to this PCC fly ash is produced in the nearby Puertollano PCC power plant with the consequent low transportation cost in case of successful Ni removing process with this combustion residue. The Puertollano PCC fly ash is characterized by a relatively high metal content and notably leaching

potential of Sb which may limit its application for the purposes of the present study.

IGCC slag /PCC ratios from 0.3 to 7.5 were applied. The leaching test EN-12457 was subsequently applied to the IGCC/PCC blends to determine the leachable potential of Ni and other elements.

2.4 Analysis

The pH and conductivity of the extraction and leaching solutions were determined by conventional methods. The concentration of major and trace elements in the mentioned solutions were determined by ICP-AES and ICP-MS respectively. The mineralogy of the extraction residue (slag) was analyzed by Powder XRD.

3.1. Preventive methods

3.1.1. Ni extraction with ammonia

High Ni extraction yields (186-196 mg/kg, equivalent to 50% of the bulk Ni extractable) are reached by using a 25% ammonia solution as extractant. This Ni extraction yields are attained at the current conditions of the slag cooling tank of the Puertollano IGCC plant (pH 9, 50 °C, 20 L/kg, 15-30 min). In the same conditions but at pH 12 (raw pH of the ammonia solution) the Ni extraction yields reached high but lower values (103-110 mg/kg, 27-29 %) than at pH 9. Besides Ni, other elements (Na, S, Si, K, Fe, V, As y Mo) show also a significant extraction with 25 % ammonia solution at both pH 9 and 12 and Ca and Mg at pH 9.

The resulting slag from the extraction with ammonia solution at pH 9 is made up in high proportions of Al-Si glassy matrix and salammoniac (NH_4Cl) and periclase (MgO) as major crystalline phase. Traces of pyrrhotite are also detected by XRD, corroborating that oxidation/dissolution is the main source of Ni in the ammonia leachates. The occurrence of NH_4Cl is due to the reaction of the HCl added to reach the pH and ammonia. The occurrence of MgO is most probably due to the dissolution of Mg from the glass matrix and the subsequent precipitation but this should be confirmed. The XRD spectra of the resulting slag from the extraction with ammonia at pH 12 shows traces of quartz and periclase while pyrrhotite is not

detected indicating a high dissolution of pyrrhotite.

3.1.2. Ni extraction with water

The Ni extraction test from Puertollano IGCC slag in the same conditions than in the slag cooling tank of the Puertollano IGCC plant at the 7-9 pH range and increasing the residence time (extraction time) up to 30 and 60 min give rise to an slightly acidic pH (3.9-4.3) and Ni extraction yields in the 111-126 mg/kg range (29-33 % extraction) in the slag cooling solution, similar to that obtained with a 25 % ammonia solution at pH 12. Although the relatively high Ni extraction yields, the leachable potential of Ni in the resulting slag (27-30% mg/kg extractable) is still being higher than the limit of non-hazardous material (19 mg/kg) for landfilling according to EC/33/2003 Decision. Furthermore the pH of the resulting slag leachates (4.7-5.2) is below the pH limit established by the above mentioned decision (6).

3.2. Corrective methods

3.2.1. Mixture of IGCC slag with alkaline materials (PCC fly ash)

Blending IGCC Puertollano slag with a lime-rich FA results in a high reduction of the leachable potential of Ni with respect to that produced in the raw IGCC slag. The leachable potential of Ni (0.02-0.1 mg/kg) is below the limit for inert material (0.4 mg/kg) established by the EC/33/2003 Decision for landfilling for all IGCC slag/PCC FA ratios investigated (0.3-0.7). Nevertheless the leachable levels of Mo and Cr give rise to classify the IGCC slag blend as non-hazardous material.

The slag blend is then a non-hazardous material with low doses of PCC fly ash (133 kg of PCC fly ash for 1tn of IGCC slag) and may be used for most of the aforementioned applications. According to the slag production in the Puertollano IGCC plant (20tn/h), 65 kg/day of PCC fly ash are required for blending.

Blending Puertollano IGCC slag with Puertollano PCC fly ash, high reduction of leachable N is also produced (0.1-93 mg/kg) with respect to that of the raw IGCC slag. By applying IGCC slag/Puertollano PCC fly ash ratios from 0.3 to 0.5 Ni extractable are below the limits for inert material established by the EC/33/2003

Decision and slightly higher (0.5 mg/kg) but very close to inert limit with IGCC slag/Puertollano PCC fly ash ratios of 0.7. Higher ratios (>1) 1:1 and 1:2 the Ni extractable contents are still higher than the limit of hazardous material.

Although the low leachable potential of Ni at ratios >0.7, the high mobility of Sb in the Puertollano PCC fly ash and the slightly alkaline pH of the IGCC /PCC blend leachates give rise to Sb leachable levels (1.6-2.9 mg/kg) higher than the EC Decision limits for non-hazardous (0.07 mg/kg) at IGCC /PC fly ash ratios >1.0., leading to classify the IGCC fly ash slag blend as a hazardous material.

The optimal IGCC slag/Puertollano PCC fly ash is in the 1-2 range, allowing classifying IGCC slag as a non-hazardous material.

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