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(54) Title: PROCESS FOR THE REMOVAL OF COBALT FROM FISCHER-TROPSCH PROCESS WATER

(57) Abstract: The invention provides a process and a plant for reducing cobalt content contained in Low Temperature Fisher-Tropsch process water. The process includes the steps of: adding a hydroxide salt or solution to the Low Temperature Fisher-Tropsch process water to form cobalt hydroxide precipitate; allowing the hydroxide precipitate to settle; and separating the supernatant with reduced cobalt from the precipitate.

Title: Process for the Removal of Cobalt from Fisher-Tropsch Process Water

Technical field of the invention

This invention relates to a process and plant for reducing cobalt contained in Low Temperature Fisher-Tropsch process water.

Background to the invention

Process water from a Low Temperature Fisher-Tropsch plant typically contains about 0.3 mg/l cobalt from the cobalt based Fisher-Tropsch catalyst. The Low Temperature Fisher-Tropsch process water is normally acidic and may leach cobalt from the Low Temperature Fisher-Tropsch solid catalyst. However, during start-up of a Low Temperature Fisher-Tropsch plant or during unstable Fisher-Tropsch process conditions the cobalt contents of the process water can be as high as 10 mg/l. Due to the negative environmental impact of high cobalt levels in process water which is returned to the environment, it is an object of this invention to provide a cost effective process for the reduction of the cobalt content of Low Temperature Fisher-Tropsch process water. Anaerobic digestion can be used to reduce the cobalt content of Low Temperature Fisher-Tropsch process water. However, this method may not always be available or effective such as when the process water also contain high levels of wax.

General description of the invention

According to a first aspect of the invention there is provided a process for reducing cobalt content contained in Low Temperature Fisher-Tropsch process water, the process including the steps of:

adding a hydroxide salt or solution or hydroxide forming salt or solution to the Low Temperature Fisher-Tropsch process water to form cobalt hydroxide precipitate;

allowing the cobalt hydroxide precipitate to settle; and

separating the supernatant with reduced cobalt content from the precipitate.

The cobalt in the process water may be in the form of Co^{2+}, Co^{3+} and/ or Co^{2+} and Co^{3+} ions.

The process may include a step of mixing the hydroxide salt or solution or hydroxide forming salt or solution to the Low Temperature Fisher-Tropsch process water.

The hydroxide salt may be sodium hydroxide and the hydroxide forming salt may be calcium oxide. Although other hydroxide or hydroxide salts would be effective, the applicant has found that the use of sodium hydroxide and calcium oxide is a cost effective and environmentally safe.

Sodium hydroxide solution may be added in a continuous manner, in line, to the Low Temperature Fisher-Tropsch process water, to increase mixing efficiency, before the process water enters a reservoir where the precipitate is allowed to settle.

The pH may be maintained at 7 or higher, preferably at about 8.5.

The process may further include the step of neutralising the cobalt hydroxide precipitate and the step of fixating the cobalt in the form of water insoluble Co_2O_3 and Co_2O_4. The fixated cobalt is more manageable and environmentally more acceptable than hydroxide salts of cobalt. Dehydration may be one way of fixating the cobalt.

After adding the hydroxide salt or solution or hydroxide forming salt or solution to the Low Temperature Fisher-Tropsch process water, the temperature of the Low Temperature Fisher-Tropsch process water, the mixture formed, may be increased in the reservoir where the precipitate is allowed to settle, to increase the settling rate. The temperature may preferably be raised above 25 deg C.

The floor of the reservoir where the precipitate is allowed to settle, the settling tank, should be conical to allow for efficient precipitate sludge, removal via a bottom valve.

The treatment of wastewater may alternatively be run on a continuous basis in a “clarifier” type vessel. The vessel should have a conical shaped settling chamber were the settled precipitate settles towards the centre of the vessel whereby it can be recycled into the influent stream or drained via a bottom valve.

After separating the supernatant, the method may include a precipitate sludge-dewatering step using a filter such as a filter press.

The cobalt sludge can be disposed of by conventional land filling. Cobalt containing sludge can also be recycled via conventional catalyst recovery or cobalt metal recovery.

The supernatant may be neutralised or its pH adjusted for further use, disposal or recycle in the plant with an acidic solution.

The quantity of the hydroxide salt or solution or hydroxide forming salt or solution may be selected such that the concentration of cobalt in the supernatant is less than 0.1 milligrams per litre (mg/l) of supernatant. Less than 0.022 milligram of calcium oxide may be used for 15 ml of process water. Less than 0.2 millilitre of 10% sodium hydroxide may be used for 15 ml of process water.

The supernatant water, substantially free of cobalt could be discarded to the environment or used as process feed water for industrial cooling. The Chemical Oxygen Demand (COD) of such cooling water should be below 50 mg/l in order to avoid organism growth in the cooling systems. COD would depend largely on the composition of the water and the influence that the process had thereon. Should the COD be above 50 mg/l the cooling water could be treated via biological processes such as anaerobic digestion, aerobic digestion or combination of both treatments to reduce the COD.

According to a further aspect of the invention, there is provided a plant for reducing cobalt contained in Low Temperature Fisher-Tropsch process water, which plant includes:

a mixing zone for mixing a hydroxide salt or solution or hydroxide forming salt or solution with the Low Temperature Fisher-Tropsch process water to form cobalt hydroxide precipitate; and

a precipitation reservoir for allowing the cobalt hydroxide precipitate to settle.

The precipitation reservoir may be provided with an overflow or drainage valve to separate the supernatant from the settled or fixated precipitate.

The precipitation reservoir may preferably be provided with a conically shaped.

In the case of continuous water treatment, the precipitation reservoir may preferably be a "clarifier" type vessel. The vessel should have a conical shaped settling chamber were the settled precipitate settles towards the centre of the vessel whereby it can be recycled into the influent stream or drained via a bottom valve.

The mixing zone may be in a conduit in the case of in line mixing of the hydroxide salt or solution or hydroxide forming salt or solution with the Low Temperature Fisher-Tropsch process water or a mixing tank.

Detailed description of the invention

The invention is now described by way of example.

Process water produced in a 1000 bbl Low Temperature Fisher-Tropsch pilot plant was investigated. It was determined that typical cobalt content of the process water during start up or unstable conditions are about 3.2 mg/l.

Calcium Oxide

Aliquots of 15 ml process water were treated with varying masses of CaO and left for a 12-hour standing period. Post treatment pH's were in the alkaline region. A precipitate formed in all the aliquot mixtures upon standing for at least 12 hours. Cobalt concentrations in the supernatant were determined with the aid of flame atomic absorption.

Results

Once the precipitate had settled out (post 12-hours) the supernatant was sampled and tested for cobalt content. Results are tabulated in the Table 1 below, cobalt concentration in the water phase being indicated in mg/l.

Table 1

Sample	CaO (mg)	Co concentration in supernatant (mg/l)	Volume process water (ml)
Blank	0.000	3.2	15.0
Sample A	0.022	<0.1	15.0
Sample B	0.035	<0.1	15.0
Sample C	0.052	<0.1	15.0
Sample D	0.114	<0.1	15.0

Sodium Hydroxide (10%)

Aliquots of 15 ml process water were treated with varying volumes of 10% Sodium Hydroxide (NaOH) and left for a 12-hour standing period. Post treatment pH's were in the alkaline region. A precipitate formed in all the aliquot mixtures upon standing for at least 12 hours. Cobalt concentrations in the supernatant were determined with the aid of flame atomic absorption.

Results

Once the precipitate had settled out (post 12-hours) the supernatant was sampled and tested for cobalt content. Results are tabulated in the Table 2 below, cobalt concentration in the water phase being indicated in mg/l.

Table 2

Sample	NaOH (ml)	Co concentration in supernatant (mg/l)	Volume process water (ml)
Blank	0.000	3.2	15.0
Sample A	0.100	3.4	15.0
Sample B	0.200	<0.1	15.0
Sample C	0.300	<0.1	15.0
Sample D	0.400	<0.1	15.0

Reaction Mechanism

Co^{2+}*(aqueous)* + 2 OH^- *(aqueous)* $\longrightarrow$ $Co(OH)_2$ *(blue solid - slowly changes to pink)*

For continuous water treatment cobalt containing feed water to this vessel is mixed with the reactant (sodium hydroxide or calcium oxide mixture, in the case of milk of lime the SG is typically 1.3) in the above mentioned example ratios and enters the “clarifier” type vessel through a central (axial) internal reaction chamber. Flow in the internal reaction chamber is up flow allowing the precipitate to form, the water then flows from the internal reaction chamber over into an intermediate chamber with a downward directed flow towards the bottom of the conical section allowing the precipitate to settle out by gravitation. Precipitation sludge at the bottom of the reactor slides along the conical floor towards the centre enabling removal via the bottom valve. Cobalt free supernatant (effluent) from the clarifier will exit the reactor via an overflow system.

This water is then treated with conventional water treatment technologies; this includes neutralisation with 20% sulphuric acid solution and filtration through sand filters.

It shall be understood that the examples are provided for illustrating the invention further and to assist a person skilled in the art with understanding the invention and are not meant to be construed as unduly limiting the reasonable scope of the invention.

Claims

1. A process for reducing cobalt content contained in Low Temperature Fisher-Tropsch process water, the process including the steps of:

adding a hydroxide salt or solution or hydroxide forming salt or solution to the Low Temperature Fisher-Tropsch process water to form cobalt hydroxide precipitate;

allowing the cobalt hydroxide precipitate to settle; and

separating the supernatant with reduced cobalt content from the precipitate.

2. A process as claimed in Claim 1, which includes a step of mixing the hydroxide salt or solution or hydroxide forming salt or solution to the Low Temperature Fisher-Tropsch process water.

3. A process as claimed in Claim 1 or Claim 2, wherein the mixing step is conducted in a mixing zone selected from a precipitation reservoir or a mixing tank.

4. A process as claimed in Claim 1 or Claim 2, wherein the mixing step is conducted continuously, in line, in a mixing zone.

5. A process as claimed in any one of the previous claims, wherein the hydroxide salt is selected from sodium hydroxide

6. A process as claimed in any one of the previous claims, wherein the hydroxide forming salt is selected from calcium oxide.

7. A process as claimed in any one of the previous claims, wherein the formed mixture is maintained at a pH of between about 7 and 8.5.

8. A process as claimed in any one of the previous claims, which includes the step of neutralising the cobalt hydroxide precipitate and the step of fixating the cobalt in the form of water insoluble Co_2O_3 and Co_2O_4.

9. A process as claimed in any one of the previous claims, wherein the temperature of the formed mixture is maintained a 25 degrees Celsius or higher.

10. A process as claimed in any one of the previous claims, wherein after separating the supernatant, the method includes a precipitate sludge-dewatering step using a filter.

11. A process as claimed in any one of the previous claims, wherein the supernatant is neutralised or its pH adjusted for further use, disposal or recycle in the plant with an acidic solution.

12. A process as claimed in any one of the previous claims, wherein the quantity of the hydroxide salt or solution or hydroxide forming salt or solution may be selected such that the concentration of cobalt in the supernatant is less than 0.1 milligrams per litre (mg/l) of supernatant.

13. A process as claimed in any one of the previous claims, wherein the supernatant water is treated via biological processes such as anaerobic digestion, aerobic digestion or combination of both treatments to reduce the COD to below 50 mg/l.

14. A plant for reducing cobalt contained in Low Temperature Fisher-Tropsch process water, which plant includes:

a mixing zone for mixing a hydroxide salt or solution or hydroxide forming salt or solution with the Low Temperature Fisher-Tropsch process water to form cobalt hydroxide precipitate; and

a precipitation reservoir for allowing the cobalt hydroxide precipitate to settle.

15. A plant as claimed in Claim 14, wherein the precipitation reservoir is provided with an overflow or drainage valve to separate the supernatant from the settled or fixated precipitate.

16. A plant as claimed in Claim 14 or Claim 15, wherein the precipitation reservoir is provided with a conically shaped floor.

17. A plant as claimed in any one of claims 14 to 16, wherein, in the case of continuous water treatment, the precipitation reservoir is a "clarifier" type vessel having a conical shaped settling chamber were the settled precipitate settles towards the centre of the vessel whereby it can be recycled into the influent stream or drained via a bottom valve.

18. A plant as claimed in any one of claims 14 to 17, wherein, the mixing zone is selected from a conduit, in the case of in line mixing, and a mixing tank.

19. A process for reducing cobalt contained in Low Temperature Fisher-Tropsch process water substantially as described herein.

20. A plant for reducing cobalt contained in Low Temperature Fisher-Tropsch process water substantially as described herein.