

Materials Selection for Bitumen with Heavy Naphthenic Acid in Canadian Oil Sands

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ABSTRACT

Canada's oil sands contain one of the largest reserves of oil in the world. According to recent estimates, there are nearly 180 billion barrels of oil in the Canadian oil sands trapped in a complex mixture of sand, water and clay. More than 40 companies have been currently operating or developing oil sands facilities since the first production in 1967.

Current oil production from the oil sands is approximately 1 million barrels per day with 3 million barrels per day forecast by 2015. The produced bitumen requires upgrading before it can be fed into conventional refineries due to undesirable octane value, sulfur contents, chloride contents, coke, other impurities, and heavy viscosity.

The process of oil sands upgrading is similar with downstream refinery, but the corrosion environment in upgrading refinery is often more severe than in the refinery because of high chlorides, mineral contents, carbonic acid, heavy viscosity and fouling, higher naphthenic acid [NA-R(CH₂)_nCOOH], and greater sulfur contents.

Naphthenic acid corrosion (NAC) which is one of the most critical corrosion issues in up & downstream refinery plants was observed for the first time in 1920's in refinery distillation processes of Rumania, Azerbaijan (Baku), Venezuela, and California. As a first API report, the 11th annual meeting stated sources and mechanism of NAC in early 1930's. API has been developing the risk base standards, such as API RP580, 571, and Publication 581 which are based on the worst NAC damage in the world since 2000.

Nevertheless not only the NAC phenomena and control in Canadian oil sands process are not much widely known but also there are still no engineering guidances for the Canadian oil sands in API standards.

This paper will give NAC phenomena and materials selection guidance against NA environment in Canadian oil sands upgrading processes.

Keywords: naphthenic acid (NA), NAC, materials selection, stainless steel, sulfur (S), molybdenum (Mo), oil sands, refining, erosion, AGO (atmospheric gas oil), LVGO/MVGO (light & medium vacuum), HVGO (heavy vacuum gas oil), SAGD (Steam Assisted

Gravity Drainage), mpy (mils per year)

INTRODUCTION

Although having been studied for approximately 80 years, NAC continues to be a problem in the refinery industry; its mechanism and how different variables affect it are not completely understood. NAC and high temperature crude corrosivity in general is a reliability issue in refinery distillation units. The presence of NA and sulfur compounds considerably increases corrosion in the high temperature parts of the distillation units. The difference in process conditions, materials of construction and blend processed in each refinery and especially the frequent variation in crude diet increases the problem of correlating corrosion of a unit to a certain type of crude oil.

The influence of NAC at 221-399°C (430-750°F) in several fired heaters, piping systems and a vacuum tower have been assessed. Typically, the higher the acid content, the greater the sensitivity to erosion-corrosion in areas of high wall shear stress. The characteristic attack is frequently observed in locations of high shear stress (erosion-corrosion), such as elbows and thermowells, and generally is more severe where the physical state of the acids is changing (vaporization or condensation). The higher NA produces more severe corrosion.

There are several methods for the determination of organic acid concentrations. The typical evaluation is by a caustic titration technique (using potassium hydroxide, KOH) to produce Total Acid Number (TAN), also called Neutralization Number, which are expressed as milligrams of KOH required to neutralize the acidity in one gram of oil. There are two standard ASTM tests for TAN measurement, ASTM D974 (a colorimetric titration method) and ASTM D664 (potentiometric titration method).

Traditionally there are at least three corrosion environments in refinery plants where NAC has been a problem:

(i) furnace tubes and transfer lines (for atmospheric column and vacuum column) where erosion-corrosion is dependent on velocity and vaporization and is accelerated by NA.

(ii) vacuum column where corrosion occurs at acid boiling temperatures, is independent of velocity and increases with NA concentration; mainly in light and heavy vacuum gas oil (LVGO & HVGO) and vacuum residue at higher than 200°C (392°F).