

COQG Q & A Panel

San Francisco, CA
31 October 2007

San Joaquin Valley Crude

- Limited data show that Se and TAN have increased in SJV. From April 2006 to February 2007, TAN data showed an increase from 0.42 to 0.63 mg KOH/g
- As SJV is a mix of different fields, the increase could be due to a change in the overall proportion of the different fields.

San Joaquin Valley

- **Q.1.** Have others seen increases, and are further changes to be expected?
- **Q.2.** With the decline in production of SJV crude, what are potential replacement crude oils?
- **Q.3.** Is anything being done to boost production from these older fields?

Selenium

- Refiners in California must monitor Se, but when opportunity crude oils are offered on the market they seldom have any data. The same can be said for Hg and Ca.
- The specification limits in some locations is 3 ppb. In others there is no limit, and often results are reported as <50 ppb.

Selenium

- **Q.4.** Should Se be an added measurement, and if 'yes', how accurate is the result expected to be? What analytical technology is available? What are the sampling and analysis protocols? Does it matter if it is organic or inorganic? Are standards available?
- **Q.5.** What are acceptable levels and tolerances?

Mercury

- There is emphasis in the Bay Area to better understand mercury in refinery streams. One agency is pushing for mass balance of mercury, starting with crude oil and going all the way to finished products, effluents, and fuel gas streams. One consequence could be that refiners must understand mercury in crude oil much better.

Mercury

- **Q.6.** What is known about distribution of Hg in crude oil, products, emissions, and effluents? What are “acceptable” levels?
- **Q.7.** What methods are available for accurately quantifying Hg in the various streams

Quality Measurement

- **Sediment & water determination by centrifuge.** It has been observed that some technicians are calling a black "glob" in the bottom of centrifuge tubes "sediment", when it is suspected it is hydrocarbon. Strictly speaking, material that accumulates in the bottom of the tube is correctly termed sediment, but it may be a mixture of organic hydrocarbon and inorganic sediment.
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- **Sub-sampling.** Another problem with the centrifuge procedure for both condensate and heavy crude oils is in trying to run the test by pulling a sub-sample out of a 1 quart can. When the sample is pulled directly from a circulating closed sampling system into the centrifuge tubes, a representative sample is obtained. When you fill a can from that sampling system, store the can, and later decide to do a water by centrifuge test errors are introduced. This should not be done, but the method does not indicate that it is not acceptable. First, the can is put in an oven (with the lid cracked to prevent pressure buildup) to heat it enough so that it will be pourable. Then it is homogenized. Then it is poured into the centrifuge tubes which is difficult to do. Potential sources of error are water (or significant hydrocarbon) boil off in the oven if the temperature is too high and/or the technician leaves it in there while at lunch. It is not homogenous and much of the water remains on the bottom of the can. Shaking by hand will not suffice, especially for lighter condensate type crude oils. If it is homogenized, then this also presents a problem. It will usually create somewhat of a stable emulsion that the centrifuge procedure will not be able to break out. And the homogenizer can heat up the crude to the point that you will boil off material. Trying to get the homogenized sample from the can to the centrifuge tube is not easy and if a little too much is "poured" over, you can't pull a little out as has been seen done. When you pour over the hot crude, the volume will change after it cools. How do you know how much to pour while it is hot? There are a lot of potential errors using this procedure.
- While Karl Fischer is not perfect and there are many ways to go wrong, it is thought to have less potential for error. But, the Karl Fischer method needs to be modified to apply to crude oils with an API gravity of $<10^\circ$.

Quality Measurement

- **Q.8.** How can a heavy hydrocarbon be distinguished from sediment in the tip of a centrifuge tube?
- **Q.9.** Is there a standard protocol for obtaining a representative sample of a heavy crude oil (API $<10^\circ$) and for accurately determining its water and sediment content? How should condensates be handled so as to not create emulsions?

Pipeline Issues

- A few systems are known to carry crude oils that are inherently incompatible.
- **Q.10.** How is this being addressed and handled by the mid- and down-stream?
- **Q.11.** What are the sources of high BS&W in pipelines carrying California crude? How is this being managed?

ANS Production

- **Q.** What are the affects of ANS tank cleaning in Valdez (macerated tank sediment in cargoes) on quality and handling of delivered cargoes? Does this contribute to 'difficult to desalt' chlorides?
- **Q.** With declining ANS production, what replacement crude oils are likely to land on the West Coast?

Production additives

- Some laboratories are experiencing problems in measurement accuracy and quality determination that impact operations. Among these are determination of API gravity and water. Some of these problems are thought to be due to additives.
- **Q.14.** What types of chemicals are used in production of crude oils in California? What is known about their effects on determination of water and API gravity?

Commingling

- **Refinery PZQ:** Among the problems that arise are asphaltene drop-out when light and heavy materials are commingled. This may not happen or become evident until the commingled crude oil reaches the refinery. Determining API Gravity (using a hydrometer) on commingled crude oils that contains very light material to "dilute" the heavy crude oils can result in the top surface "boiling" for more than the 5 minutes. While it is recommended allowing the crude oil mixture to stabilize in the open cylinder this results in loss of light material and a lowering of API Gravity. Commingling crude oils with different chemical additives can lead to incompatibility reactions such as emulsion formation.
- **Refinery JYW:** Crude compatibility, specifically asphaltene precipitation, continues to be a challenge as we see crude oils we've never experienced before. At our refinery we pre-test crude oil diets to try and get a handle on mixing crude oils from all over the place. While most crude mixes seem to be functional from the compatibility standpoint, there are times where we are pretty close to the edge. Of course, the assumption is that the evaluation samples we receive are truly representative of the proposed crude oil.

Commingling

- **Q.15.** How are these issues being handled and managed?

Stripper Production

- Many California fields are small, with *mom and pop* operations producing only a few bbls per day. These are stored in tanks until they become full, then a truck collects and discharges the production into the nearest pipeline.
- **Q.16.** How is quality consistency and reliability of crude oil gathered in this way being addressed? What about commingling and compatibility of receipts from widespread tanks?

Synthetic Crude Oils

- Growing supply of tar sand synthetic crude oil streams is creating its own problems. Their high solids content wreaks havoc with desalters by forming emulsions. It is difficult to predict solids ahead of time because getting a representative sample is difficult. Then mixing in the laboratory has to be very good or again your sample is not representative.

Another problem with synthetics is the addition of cutter stocks to these streams by the pipeline. Low grade cutters can have high concentrations of H₂S, with significant impacts when received at the refiner's wharf. This happened to us recently. After some investigation the pipeline in Canada told us it was common for them to add high sulfur cutters. Needless to say, different batches had different levels of H₂S and caused us considerable grief.

- **Q.17.** Are other experiencing these problems and, if so, how are they being handled?