On-line rolling oil and pickling acid concentration measurement using ultrasonics

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INTRODUCTION

The measurement of the speed of sound through a liquid has found many applications for the determination of concentration in chemical solutions. The measurement is a repeatable physical constant of the liquid. Because the sensors are not in direct contact with the liquid, have no moving parts, and may be constructed out of many different materials, this technology has proved especially useful in harsh environments and on-line applications. Minimal maintenance or calibration is required.

This technology was developed shortly after WW II by ex-navy sonar personel. Industrial applications where first performed over twenty five years ago, and at this time there are hundreds of sound velocitimeters installed in a large assortment of applications.

Technological improvements have yielded very precise equipment. Today's sound velocimeters are repeatable to 0.10 meter/second, with a resolution of 0.01 m/sec. Since sound velocity through a liquid is related to the density of the liquid, a comparison to more commonly know density measurements can show how sensitive this method is. The density of water changes by 0.00116 gm/ml for a 5° C temperature change. This also results in a sound velocity change of 14.34 m/sec. Thus the 0.10 m/sec repeatability equates to a densitometer with a repeatability of 8.2E-06 gm/cc.

The sensor used for measuring the speed of sound consists of two piezo-crystals. One transmits a pulse of sound through the liquid. This pulse bounces off a reflector and returns to the second crystal. The electronic hardware determines the time elapsed between transmission and reception of the pulse. From prior calibration, the acoustic pathlength is known, and this distance divided by the time yields the sound velocity. Sound velocity, like many other physical characteristics, is affected by temperature, therefore, an RTD temperature sensor is also incorporated in the sound velocity sensor (see Fig. 1). The standard material of construction is stainless steel, and alloys such as the Hastelloys or Carpenter 20 are also available. The standard process mounting of a sound velocity sensor is on a 2" 150# ANSI flange. This requires either a 2" "Tee" or a 2" riser at the location to be monitored. Many other mounting options are also available.

CONCENTRATION MONITORING

The speed of sound will typically change as the liquid changes. If the liquid contains some substance dissolved in a solvent, and its concentration changes, this will usually be reflected as a change in sound velocity. *Graph #1* shows sound velocities vs. concentration for some common chemicals. The response of sound velocity and temperature vs. concentration can

be programmed into an instrument. This allows the instrument to directly calculate the concentration of the chemical in question. The accuracy of the measurement depends on the precision of the sound velocity measurement and the slope or steepness of the response curve.

There is no requirement that the liquid be conductive, that the solvent be water, or that the temperature be moderate. There are two requirements for a succesful measurement: the sound velocity must change when (and preferably only when) the concentration changes, and the liquid must be sonically transparent.

Most liquids are sonically transparent. The most common cause for sonic opaqueness is bubbles in the liquid, either gas or second phase liquids. Bubbles cause the sound pulse to disperse, making the measurement difficult. Undissolved or suspended particles can also cause problems.

Sonic concentration monitoring normally works best when the liquid is binary, that is, contains one thing dissolved in one solvent. If there is more than one variable to be measured, changes in the concentration of the other variables can shift the sound velocity, causing a measurement error.

ROLLING OILS

As can be seen on *Graph 1*, rolling oils exhibit changes in sound velocity which correlate to their concentration. The actual sound velocity vs. concentration curves depend on the type and brand name of the oil. It is therefore customary to evaluate oil samples prior to installing an instrument. To date dozens of these sound velocity meters have been installed for this application.

The sensor installation location should be carefully evaluated. Installation on a by-pass line is desirable because flow can be restricted to the point that bubbles rise above the sensor. If the process line contains filters, locating the sensor after the filter minimizes solid particles. Is usually not recommended to install the sensor directly in a mixing vessel.

Many of the processes which use rolling oils also have a tendency to pick up secondary oils, known as tramp oils. The presence of these tramp oils can cause an error in measurement. What the effect of the tramp oil will be varies dramatically. Some cause no error, other cause error at a ratio of 1 to 1. Most tramp oils cause error at a ratio of about 3 to 1, that is, a 3 vol. % increase in tramp oil causes the measured rolling oil concentration to increase by 1 vol. %.

ULTRASONIC CHROMATOGRAPHY

In order to eliminate error associated with tramp oils, and to measure both the rolling oil and tramp oil concentrations a more sophisticated approach is needed. Ultrasonic Chromatography is a measurement method where the principle data is the changes in the speed of sound over a period of time. The method is useful when the liquid being measured consists of non-miscible components, emulsions or suspensions. A sample is held captive, and as the components in the liquid separate, the speed of sound through the liquid changes. When the separation is complete, the speed no longer changes. By quantifying the initial

velocity as well as changes in velocity, both rolling and tramp oil concentrations can be determined.

The sample chamber (Fig. 2) has two ports, an inlet and an outlet. On each side is an acoustic transducer. An RTD temperature sensor is also incorporated. The measurement of sound velocity is made only on the region between the acoustic sensors, known as the acoustic path.

The sample enters and exits the chamber utilizing process pressure. The only moving parts are the valves. Once a fresh sample has entered the chamber, the valves close and the data is recorded.

Three UC curves are shown in *Graph 2*. Data to the left of zero minutes is data while the solution is flowing and stirred. To the right of zero is when the valve are closed and the sample is blocked in. The first curve is for 5.7 % rolling oil in water. The third is for 7.0 % rolling oil in water. The shape of these curves is practically identical. Both show a slow decay as the rolling oil emulsion breaks down. The shift in sound velocity for rolling oil is 2.5 m/sec for a 1.3 % rolling oil change. Note that the sound velocity is shown as the difference from the sound velocity of pure water.

The second curve is for 5.6 % rolling oil and 4.6 % tramp oil in water. When the sample is blocked in, the tramp oil rapidly comes out of the solution (about 6 minutes in this case), and the response from then on is as expected for the rolling oil alone!

Converting the acquired data to oil concentration is straightforward. The velocity after 15 minutes of settling correlates directly to the rolling oil concentration independent from any tramp oil (See *Graph 3*). For rolling oil alone, the difference between the velocity at 0 minutes and the velocity at 15 minutes is expected to be about 1.4 m/sec. Any shift greater than this would indicate the presence of tramp oil and allow its concentration to be determined. For the data shown in *Graph 1*, a shift of 4.2 m/sec was observed, 2.8 m/sec greater than expected for a no-tramp solution.

PICKLING ACIDS

The measurement of acid concentration, specifically hydrochloric acid (HCl) can be easily performed with standard sound velocimeters. The typical HCl sound velocity probe is constructed out of PVDF (Kynar). The difficulty in measuring pickling acid is that the acid generally contains large amounts of iron salts. These salts cause shifts in the sound velocity response curves and lead to large measurement error.

In order to measure these acids, it is necessary to have a secondary measurement, a conductivity meter. Sound velocity changes a lot for the salt but a smaller amount for the acid concentration. Conductivity on the other hand changes a lot for the acid, but a smaller amount for the salt. By simultaneously measuring both sound velocity and conductivity (and temperature) both the acid and the salt concentrations can be accurately determined.

Graph 4 shows sound velocity and conductivity responses for mixtures of HCl and salt all at 20° C. Say for example that the conductivity was measured at 300 mS/cm; If the salt

concentration were 0.00 %, the acid concentration would be 8.50 % and the sound velocity would be 1493.90 m/sec.. If the salt concentration were 10.00 %, the acid would be 5.83 % and the sound velocity would be 1606.9 m/sec. By now measuring the sound velocity, the acid and salt concentrations can be precisely determined. If the velocity was measured at 1550.4 (exactly half way between the two), the salt concentration would be know as 5.00 % and the acid as (8.50 + 5.83) / 2 = 6.90 %.

SUMMARY

Sound velocity measurement has proven to be a reliable and low maintenance method for on-line analysis. Technological innovations and combinations with other methodologies have overcome many of the difficulties associated with impurities and secondary variables in the liquids.

REFERENCES

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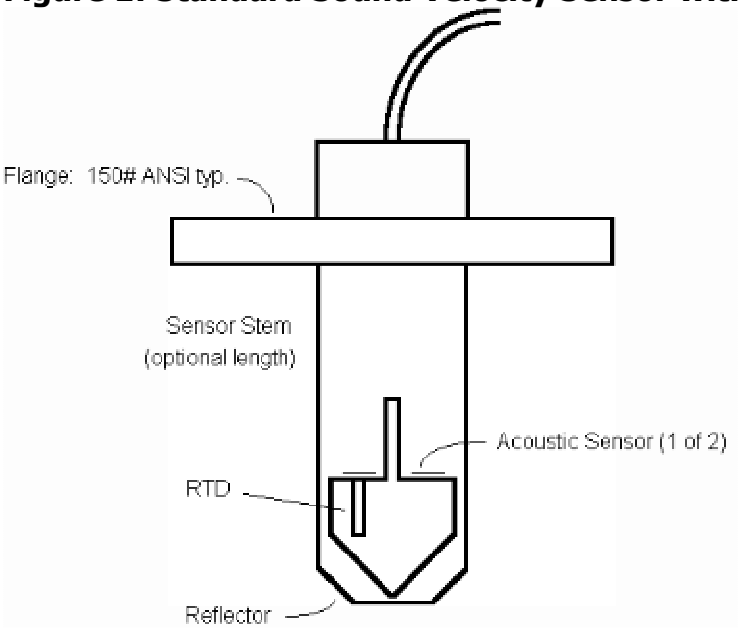
Schaaffs, W., Molecular Acoustics, Landolt-Bornstein Numerical Data and Functional Relationships in Science and Technology, Group II, Vol. 5, Springer-Verlag, New York, 1967.
Franz, D. W. and Zacharias, E. M., Sound Velocimeters Monitor Process Streams, Chemical Engineering, Jan. 22, 1973

Figure 1: Standard Sound Velocity Sensor with RTD



Graph 1: Typical Velocity Response for Assorted Chemicals

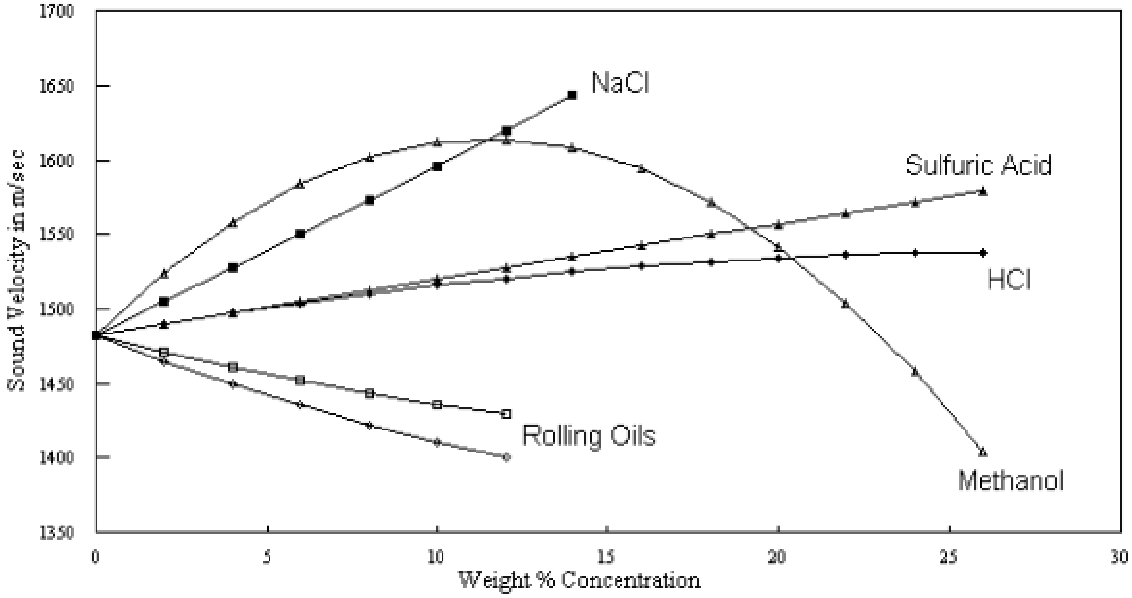
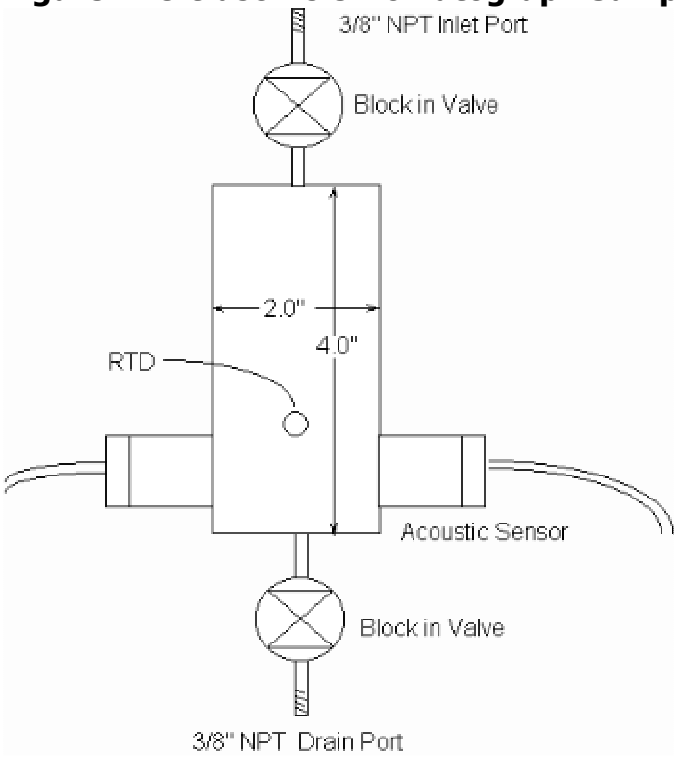


Figure 2: Ultrasonic Chromatograph Sample Chamber



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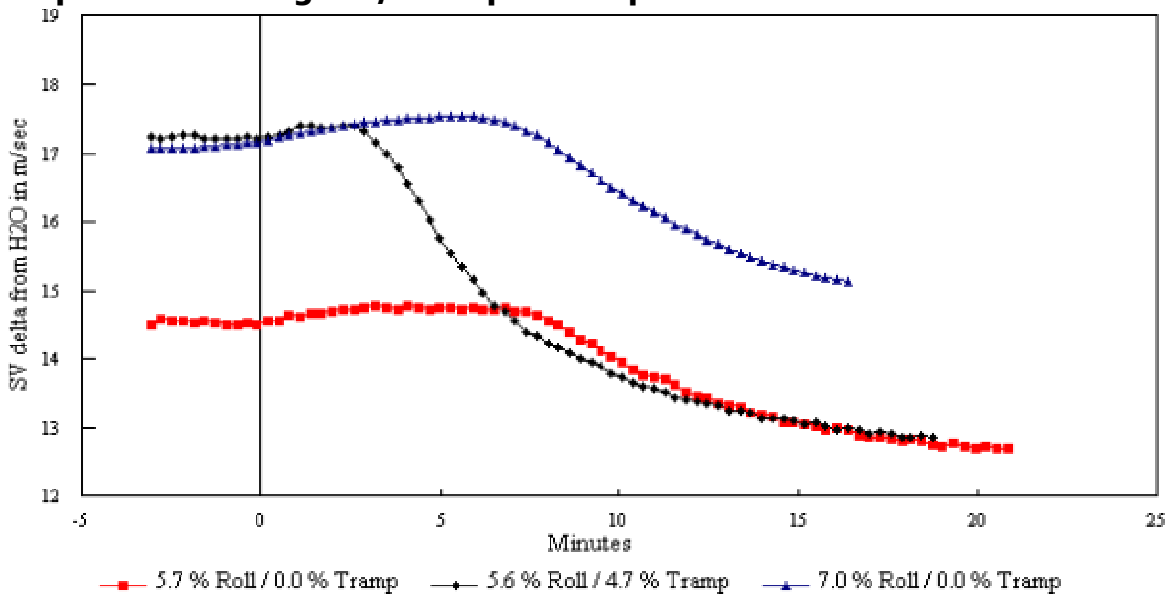
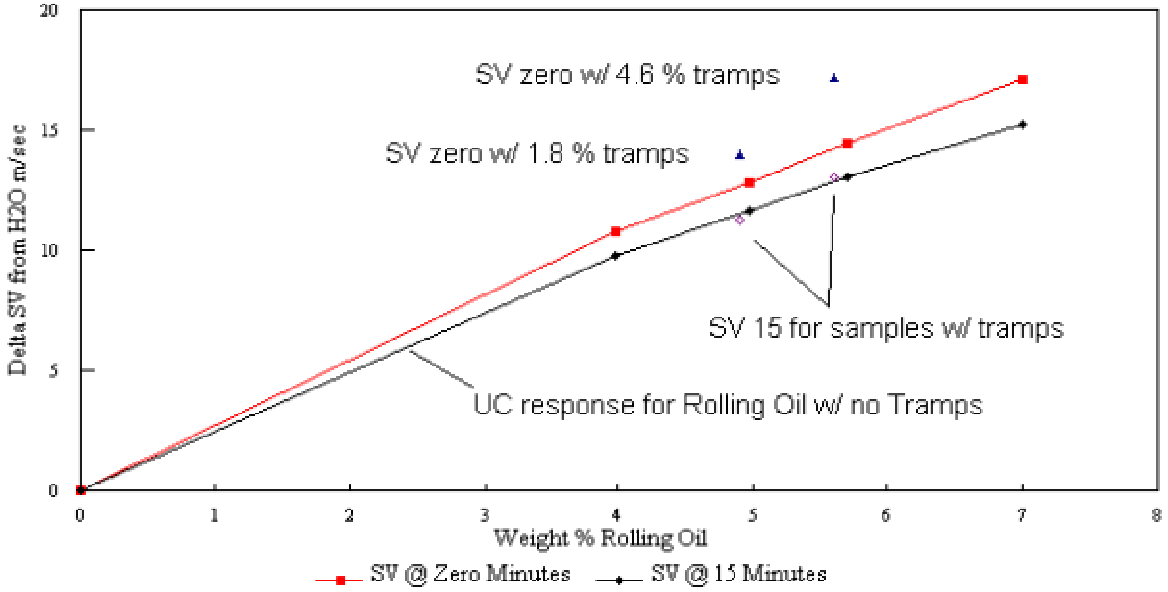
Graph 2: UC Rolling Oil / Tramp Oil Response



Graph 3: Analysis of UC Response for Rolling Oil / Tramp Oil Mixtures



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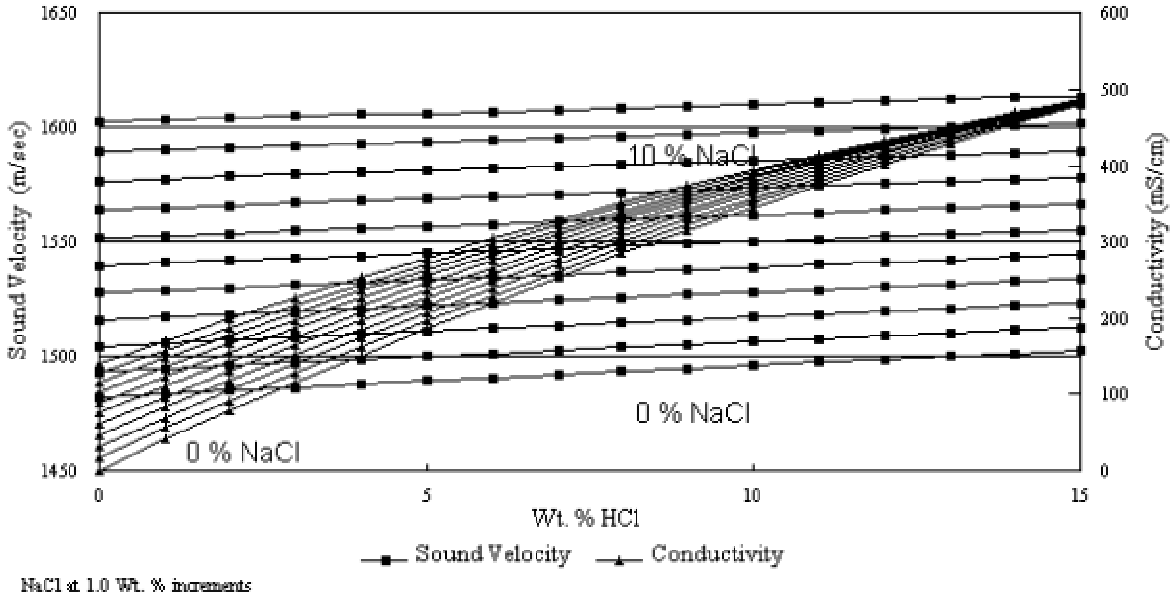
Graph 4: Sound Velocities and Conductivities for Acid / Salt Mixtures



NaCl at 1.0 Wt. % increments

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