Compensation For Temperature Variation In Ultrasonic Chemical Process Monitoring

A.N.Kalashnikov, V.Ivchenko, R.E.Challis, A.K.Holmes
School of Electrical and Electronic Engineering
The University of Nottingham,
Nottingham, NG7 2RD, UK
Alexander.Kalashnikov@nottingham.ac.uk

***Abstract*— Chemical processes often involve heat exchange that causes changes in the temperature of the reactor. These temperature changes could affect ultrasonic monitoring of the processes to the same extent as changes in chemical composition. Discrimination between these two factors requires separate monitoring of the temperature. An ultrasonic reflector for pulse-echo monitoring of aqueous solutions with integrated temperature sensing was developed, implemented and experimentally tested. It contains a water filled cavity isolated from the test medium that is used as a reference. A compact 3 mm wide cavity provides changes in propagation delay of about 1 sample per 0.05°C at a sampling frequency of 2430 MHz. The possibility of achieving even finer resolution is demonstrated.**

Keywords- ultrasonic monitoring of chemical processes, temperature sensing, integrated ultrasonic reflector

I. INTRODUCTION

Ultrasound can be employed for determining various parameters of aqueous solutions, for example, density, temperature, concentration [1], and for monitoring of chemical reactions with a sensitivity of around 300 ppm [2]. Reliable and accurate instruments should be capable of discrimination between various physical factors that cause changes in recorded ultrasonic signals. In this paper we consider discrimination between changes caused by temperature and changes caused by chemical composition on the velocity of ultrasound in aqueous solutions.

Due to the sensitivity of the ultrasound velocity to temperature in water (equivalent to around 0.2% per °C), accurate measurements of the velocity of ultrasound are predominantly performed in a purpose designed and built test cell with carefully controlled temperature (for example, [3]). The drawback of this approach is the difficulty of its application *in situ* for evolving processes that in many cases release or absorb thermal energy. This results in notable variations of temperature. Additionally, just stirring a solution that is required to keep it homogeneous could cause notable temperature rises. A provision of *in situ* measurements was a strong objective in this study.

It is possible to measure the temperature in the test medium by an additional thermo sensor (e.g, thermocouple). This approach became a standard for many conventional chemical instruments like the pH meter, where the reading is computed from the sensing electrode output and the output from a temperature sensor. This could be adopted for ultrasonic instrumentation, but it involves extra wires, electronics, processing, synchronization, and calibration. Additionally, it is not obvious where to put this sensor (near the transducer, near the reflector or somewhere in between). We aimed for an integrated ultrasonic temperature sensor capable of determining the ultrasound velocity and temperature of a medium separately from a single record.

This measurement requires part of the ultrasonic signal pathway to have fully known ultrasonic and temperature properties. A reflector of ultrasonic waves used in pulse-echo mode can be seen as a candidate for this role. (In pitch-catch mode an additional component could be placed in between the transducers to give the same effect.) A water filled cavity integrated in the reflector was used for this purpose, and this enabled the desired degree of accuracy to be achieved. The following section describes an example of compensation for the temperature influence that led to a qualitative change in the interpretation of the corrected ultrasonic data, and provided motivation for the present research. The design of the reflector is discussed, and experimental results follow. Finally, the conclusions are presented.

This research was supported by EPSRC (UK)

II. AN EXAMPLE OF THE IMPORTANCE OF TEMPERATURE CONSIDERATIONS FOR AN ANALYSIS OF ULTRASONIC DATA

Some results relating to ultrasonic monitoring of changes in chemical composition imposed by time resolved titration were reported at the previous IEEE Ultrasonics Symposium [2]. The graph showing the delay of the ultrasonic pulse versus time (fig.3, experimental curve) shows two distinct inflections around the end point of the titration, with an overall decrease in the delay time of about 60 ns. The temperature readings that were recorded alongside the ultrasonic and pH data by the pH meter (fig.1) are considered in the present study. If the solution was water with a gradient of 2.5 (m/s)/°C [4] and no changes in the chemical composition occurred, fig.3 (experimental curve) would present quite a different shape. This curve is shown in fig.2 where the overall change in the delay is about 60 ns as well. Therefore changes in temperature alone could cause effects of the same magnitude that was observed from the experimental ultrasonic data. Corrected values of delays were calculated assuming that the above mentioned value of the gradient was still applicable to the evolving solution, and the ultrasound velocity was close to 1500 m/s:

$$\tau_c(t) = \tau_e(t) + mean(\tau_e) \times \frac{2.5 \times (mean(T) - T(t))}{1500}, \quad (1)$$

where τ_c, τ_e are the corrected and experimental delays respectively, T is the recorded temperature, t is time. These corrected values are plotted in fig.3 (corrected curve) and show two almost linear slopes with different gradients that join at the end point of titration. This behavior is remarkably different from what can be observed from the raw data, and provides a much more useful insight into the formation of the precipitate in the reaction monitored. This experimental observation stimulated our interest in accurate monitoring of temperature along with the conventional ultrasonic measurements for process monitoring.

III. DESIGN OF THE REFLECTOR WITH INTEGRATED TEMPERATURE SENSING FUNCTION

In pulse echo mode the reflector directs ultrasonic waves backwards to the transducer. If a signal from a reflector's rear boundary is recorded along with a signal from the front face boundary, it is possible to measure the time difference between these two signals at different temperatures and thus calibrate it for temperature measurements. Using a relatively large reflector rather than a single point temperature sensor provides an extra advantage of some averaging of ambient temperature due

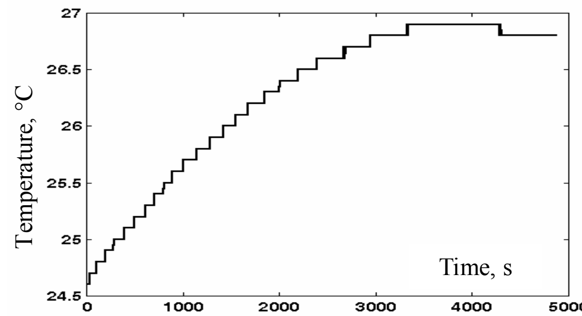

Fig.1. Temperature profile that was recorded along with the ultrasonic data

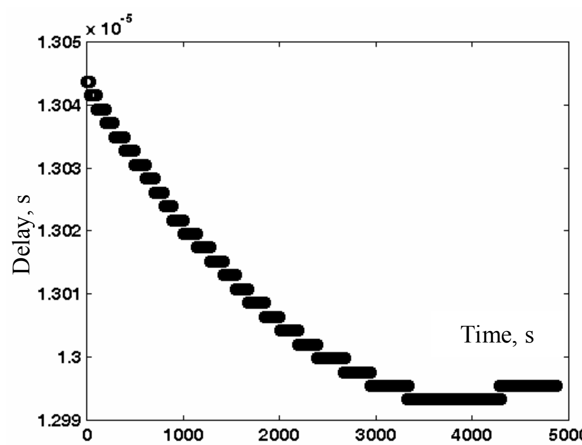

Fig.2. Simulated delay times if the monitoring solution was water with the recoded temperature

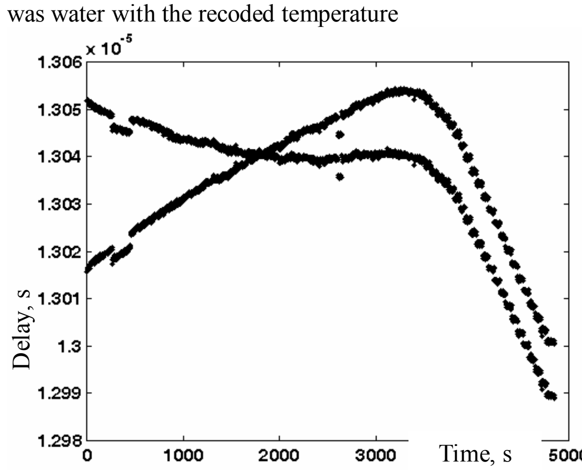

Fig.3. Experimental (from the upper left corner) and corrected delay curves

to a full thermal contact with the environment (aqueous solution under test) and a substantial surface area. However, ultrasound velocity in many solids has lower sensitivity to temperature than that of water. (This was observed experimentally for stainless steel, and some data are available for other materials, e.g. [5].) Combined with a much higher nominal velocity of ultrasound in solids than in liquids, these factors require an unacceptable width of the reflector. Hence a water filled cavity in the reflector was used that would have similar sensitivity to temperature as the test medium, retain the useful temperature averaging property of a solid reflector, and remain isolated from the medium under test not to be influenced by all the other physical and/or chemical changes in it. For the water filled cavity, several acoustic pathways will contribute to the overall received signal in the time domain (fig.4). Pathway 1 gives the strongest

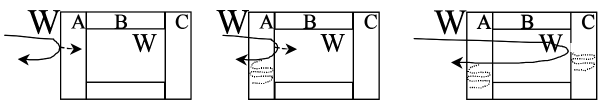

Fig.4. Acoustic pathways for reflection from the front face (1,left), from the entrance of the cavity (2, centre) and from the rear face (3,right)

signal that is of principal interest in conventional measurements. Its amplitude is proportional to

$$A_1 \propto r_{AW} = \frac{Z_A - Z_W}{Z_A + Z_W}, \tag{2}$$

where Z_A and Z_W are the acoustic impedances of the material of the front face of the reflector and water respectively. The second pathway produces a time reference signal when the ultrasonic pulse enters the cavity. Its amplitude is proportional to

$$A_2 \propto t_{WA} r_{AW} t_{AW} = \frac{4 Z_W Z_A}{(Z_A + Z_W)^2} \frac{Z_A - Z_W}{Z_A + Z_W}, \tag{3}$$

assuming the acoustic impedances of the test medium and water are close to each other for diluted aqueous solutions. As $t_{AW}<1$ it follows $A_2<A_1$. For conventional measurements A_1 is maximized by fabricating the front face from a metal that gives $Z_A>>Z_W$ thus $r_{AW} \to 1$. However this would give $t_{AW}<<1$, and the signal from the second pathway could be too weak for a reliable measurement. Analysis and numerical simulations showed that use of Plexiglas for the front face would be a much better alternative and this was confirmed by experiments. The third pathway involves reflection from the rear face with the amplitude proportional to

$$A_3 \propto t_{WA} t_{AW} r_{WC} t_{WA} t_{AW} = \left(\frac{4 Z_W Z_A}{(Z_A + Z_W)^2} \right)^2 \frac{Z_C - Z_W}{Z_C + Z_W}, \tag{4}$$

where Zc is the acoustic impedance of the material of the rear face of the reflector. A_3 was maximized by using stainless steel for the rear face ($Z_C>>Z_W$ thus $r_{WC} \to 1$). There are some additional reverberation pathways shown by dotted lines in fig.4. These were eliminated from consideration by using time domain windows.

IV. EXPERIMENTAL PROCEDURES AND RESULTS

The experimental results were obtained using a custom built ultrasonic instrument that provided an equivalent sampling rate for data acquisition of 2430 MHz combined with 256 averages in less than two seconds. A typical response recorded from the sensor with a width of the cavity of 3 mm is presented in fig.5. It shows the amplitudes of the three considered pulses were high enough to be recorded without the need to change the gain of the pre-amplifier during the measurements.

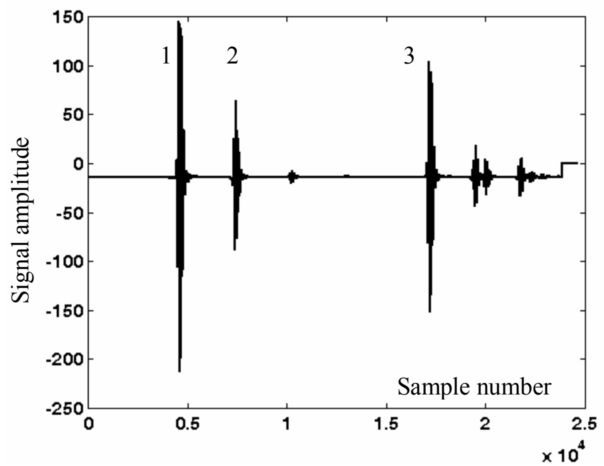

Fig.5. A typical signal recorded from the reflector with a water filled cavity, digits indicate contributions from the separate acoustic pathways (fig.4), subsequent reverberations are not labelled

Estimation of the delays between pulses 2 and 3 (that were isolated from all the other pulses using appropriate time domain windows) was made using a zero-crossing technique due to their different shapes. Sub-sample resolution of the estimated delays was implemented. Records were collected every 10 seconds for a total number of 100 samples, while the temperature in the reaction vessel rose due to the influence of a stirrer that was used to homogenize the solution under test. Fig.6 shows estimated delays in the cavity that exhibit a clear downward trend that is very close to a straight line. The recorded values of temperature are shown in fig.6 giving an idea of the sensitivity achieved by using an integrated sensor. A zoomed fragment shows 30 distinctive ultrasonic readings for the recorded change of temperature of 0.1 ^{o}C.

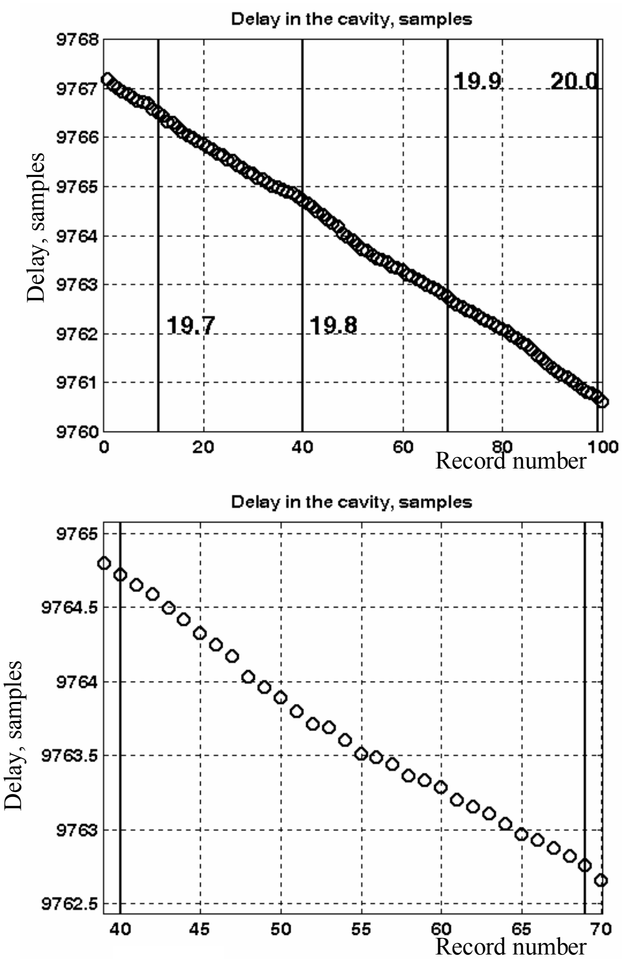

Fig.6. Estimated signal delays for 100 consecutive ultrasonic records (circles), vertical lines showing temperatures recorded using a conventional thermometer and their labels correspond to the temperatures, °C

V. Concluding Remarks

Discrimination between different factors affecting ultrasonic propagation is very important for ultrasonic process monitoring. It can be facilitated by using a reflector with a water-filled cavity in pulse-echo mode, that provides a reduction of the required reflector width. The reflector should incorporate a front wall of a material that matches the impedance of water better than metal, Plexiglas being a viable choice. Having a good thermal contact with the medium under test, use of the reflector reduces the variability of measurements due to its substantial surface area and is an added advantage. The sensitivity of temperature monitoring is proportional to the width of the reflector and sampling frequency, and can be improved by using sub-sample delay estimation techniques. Use of the developed sensor, ultrasonic instrument and signal processing procedure allowed sensing of temperature changes with a resolution more than adequate for ultrasonic process monitoring.

Acknowledgment

Mr.A.Dockar and Ms.A.Adelekun have contributed to the development through their final year projects.

References

[1] R.C.Asher, Ultrasonic sensors, Institute of Physics Publishing, Bristol, 1997.

[2] A.N.Kalashnikov, K.L.Shafran, R.E.Challis, C.C.Perry, M.E.Unwin, A.K.Holmes and V.Ivchenko, "Super-resolution *in situ* ultrasonic monitoring of chemical reactions", in *Proc. IEEE Ultrason. Symp.,* 2004, pp. 549-552.

[3] R.Belchamber, A.Brookes, J.Carey et al, "Observation of acid-base transitions by near-field active ultrasound spectroscopy", www.anamap.co.uk/pdf/acid_base_transition.pdf, 10.09.2005.

[4] V.A.DelGrosso and C.W.Mader, "Speed of sound in pure water", J. Acoust. Soc. Am., vol.52, 1972, pp.1442-1446.

[5] M.S.Skolnick, S.Roth and H.Alms, "Ultrasound measurements in the layered transition-metal dichalcogenides $NbSe_2$ and TaS_2", J.Phys.C: Solid State Phys., vol.10, 1977, pp.2523-2526.