DEVELOPMENT OF A CYANIDE CONTENT MEASUREMENT METHOD IN SALT MELTS FOR STEEL HARDENING USING RAMAN SPECTROSCOPY [†]

Andrej Stergaršek, Robert Kocjančič*
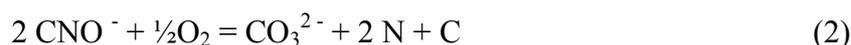
Jožef Stefan Institute, Jamova 39, Ljubljana, Slovenia

Abstract

The development of a measurement method for the determination of cyanide content in salt melts for steel hardening using Raman spectroscopy is shown. The laser beam and the signal are led through the glass fibre extension, so the sensitive measuring equipment can be in separate room from the salt bath furnaces. A method of complete sampling and measurement automatisation is also proposed.

Introduction

Novel processes for nitriding, carbonitriding and carburisation (metal hardening) of metal surfaces eliminated the by-production of toxic wastes.[1] This is accomplished by supplementing additives which regenerate the used cyanide or cyanate in the salt melt, lower the carbonate content in the melt and at the same time do not increase the content of cations in the melt which increase the amount of salt, contaminated with cyanide.[2] In order to be able to study and develop the appropriate additives it is necessary to have a reliable and quick measurement method for determination of cyanide content in the salt melt.

Nitriding and/or carburisation of a metal surface are accomplished using the same salt melt media. The preferential chemical process depends only on temperature. The reaction sheme is the same for both processes:

$$2\,CN^- + O_2 = 2\,CNO^- \tag{1}$$

$$2\,CNO^- + \tfrac{1}{2}O_2 = CO_3^{2-} + 2\,N + C \tag{2}$$

$$C + \tfrac{1}{2}O_2 = CO \tag{3}$$

Reaction (2) takes place from 540 °C by inclusion of nitrogen into the metal crystal structure, from 570 °C both nitrogen and carbon are being included and above 840 °C only carburisation (inclusion of carbon) takes place. Cyanide ions, which are added as

organic material, react with oxygen (present due to the forced air intake) to form cyanate ions (reaction (1)), which then decompose to form carbonate and elemental nitrogen and carbon (reaction (2)).

In the following we will present a comparison between a classical and a regenerative metal hardening processes. The classical approach is shown schematically in Figure 1. By inclusion of nitrogen into the metal structure the content of carbonate in the melt is increased which in due time causes the salt melt to become inactive. According to the classical process the supplement of the cyanide is achieved by elimination of a part of the salt melt and by addition of a fresh cyanide. The side-product is therefore a toxic cyanide- containing salt.
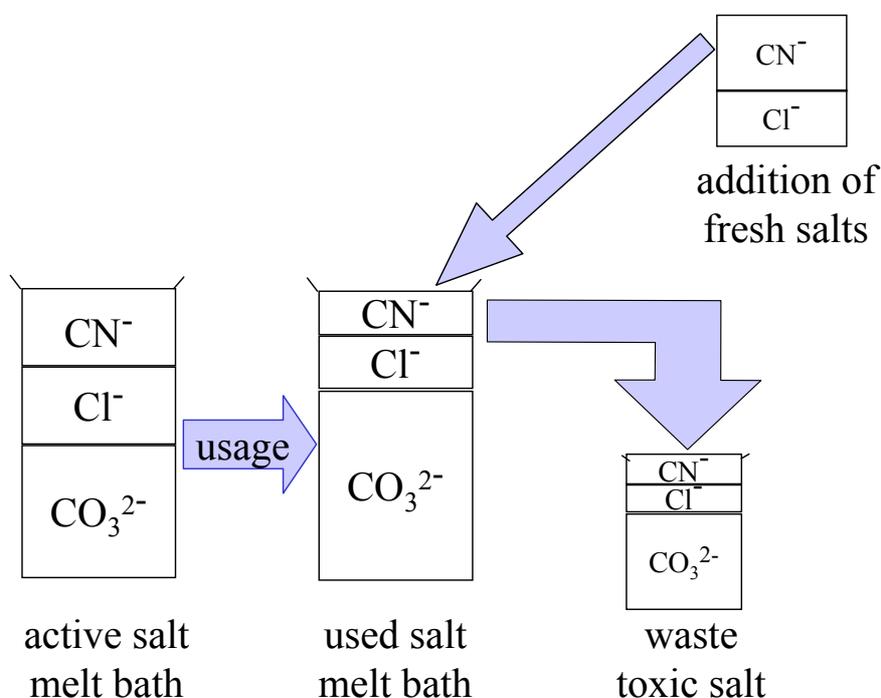

Figure 1: The classical metal hardening process: regeneration of the salt melt by subtraction of a portion of used salts and addition of fresh salts. The subtracted salts represent the water soluble toxic waste material.

The regenerative process is schematically shown in Figure 2. By addition of a suitable regenerator (which does not contain cyanide) the cyanide ion forms in the fused salt melt and the carbonate ions simultaneously decompose into water and carbon

dioxide which emanates from the salt melt system. Water vapour, as a side product, speeds-up the emanation of CO_2.
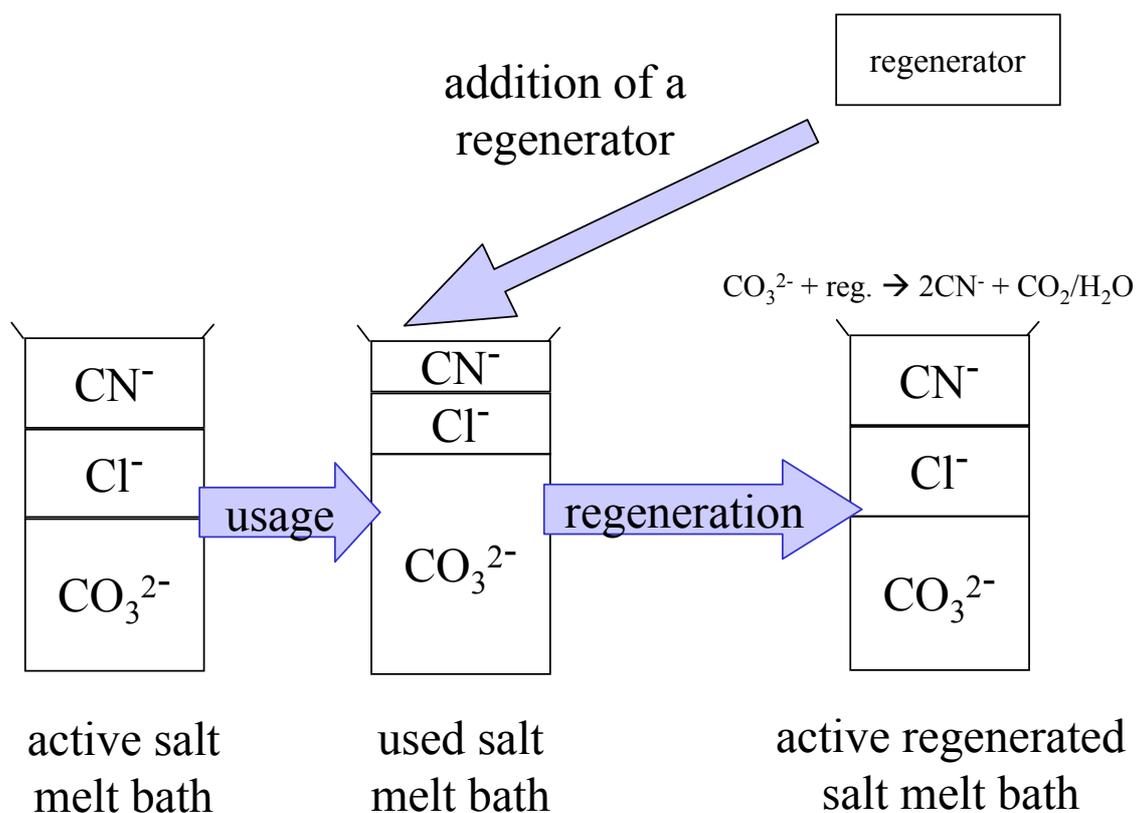
Figure 2: The regenerative metal hardening process: no toxic waste is produced and the side products are only CO_2 and water vapour.

As it can be seen from the scheme, the regenerative process does not produce toxic wastes. However, in order to maintain a fresh and active salt bath a much better control of the cyanide content in the fused salt bath is needed. Additionally, a better and automatic on-line control renders possible a more stable operating conditions and less fluctuations in the product quality.

Among the potential cyanide content test methods are chemical analysis of the cooled salt melt sample, analysis using the IR emission spectra of the hot salt melt, analysis of the IR absorption spectra of cooled salt melt and analysis of Raman spectra of hot or cool salt melt. The chemical analysis demands a permanent presence of a laboratory technician for sampling and performing the analyses. Similarly, absorption IR spectroscopy of cooled salt melts cannot be automatised since the procedure demands

grinding of the melt and mixing with nujol to form a paste. The paste must be consequently repeatably put onto a test crystal (usually NaCl) and thinned into a film of the same thickness in order for the different measurements to be comparable. If equal thickness is not achievable, an internal standard addition method must be used which is even more time and resource consuming. So, the only two potentially adequate cyanide content test methods remain emission IR spectroscopy of the hot salt melt and Raman spectroscopy of the cold salt melt.

The first of the two methods, the IR emission spectroscopy, demands a specially adapted IR spectrometer where the IR source is replaced by a surface of the hot salt melt, usually behind a quartz glass. The literature review in this field showed different approaches.[3-8] The described methods range from replacing the IR source in the FTIR spectrometer with a thin film of molten salt on an electric furnace and measuring the "background" to measuring the emission spectrum of a hot salt in the furnace using aluminium mirrors and using black body emission (the black body being at the same temperature as the salt melt sample) as a background. All described approaches produced good results but were only useful for the research applications. In order for such an equipment to be used in the e.g. tool-hardening shop, the equipment would have to be very well protected from the environmental influences (high and fluctuating temperatures, dust), so this approach has been evaluated as not feasible.

The second method, the Raman spectroscopy of the cold melt, also posed a few problems. The literature review showed two approaches,[9,10] both dealing with the measurement of Raman spectra of the melt through a quartz glass of a vessel in the furnace. Raman spectroscopy offers the possibility of using glass fibres to bring the laser beam to the sample surface and to send the Raman spectra back to the spectrometer which can be positioned in a room separated from the furnaces with the fused salt. This advantage of Raman spectroscopy prevailed in the selection of the method. For quantitative analysis the strong band at 2082 cm^{-1} is used (C≡N).

Experimental

The experimental equipment used in development of the method and the proposed automatic sampling technique is described below.

For the preparation of the test salt melts a small laboratory scale furnace was built shown schematically in Figure 3.
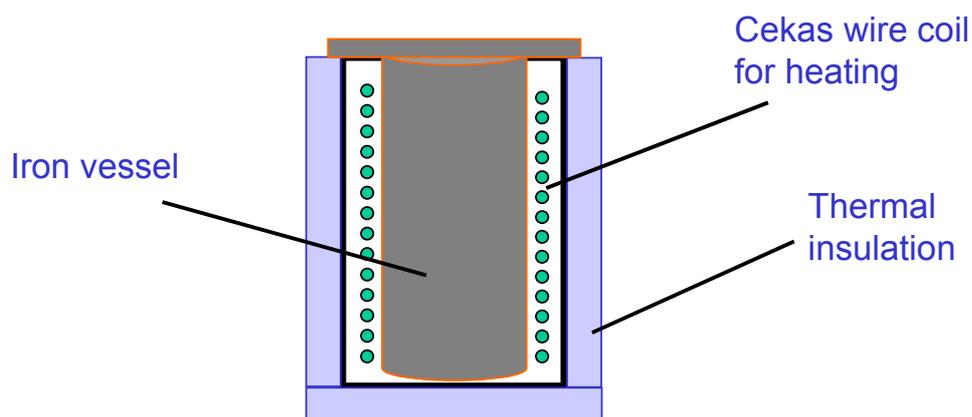

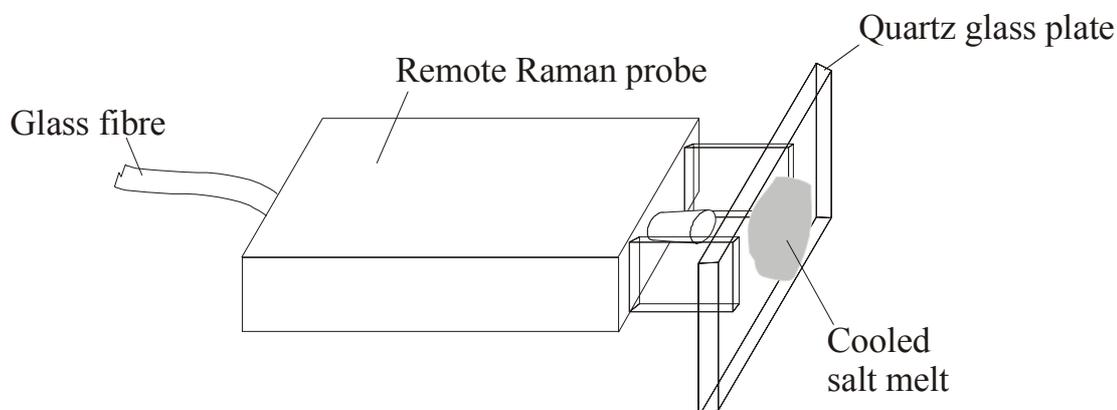Figure 3: Schematic cross-section of a 2 kg laboratory scale furnace for preparation of salt melt samples.

Figure 4: Schematic arrangement of the remote Raman probe showing the position of the sample hardened salt melt on a quartz glass plate during the measurement.

The capacity of the furnace is to heat 2 kg of salt mixture up to 1000 °C. The sample salt melts were prepared in the vessel and used for the calibration.

The fused salt melt was extracted from the furnace and poured on the plan-parallel quartz glass plate. The melt cooled quickly and the glass plate provided a smooth and flat surface of the hardened salt mixture. The measurement of the Raman spectra was performed using the glass fibre probe through the quartz glass. The focus of the laser beam was on the flat surface of the hardened salt at the interface of the salt and quartz glass. The scheme of the Raman spectra measurement arrangement using a remote probe is shown in Figure 4. Since the focus of the measured spot is set to 18 mm from the probe lens, two distance poles were used and the quartz glass plate was pressed firmly towards the poles during the measurement. In this way correct measurements were possible without repeated focusing of the beam.
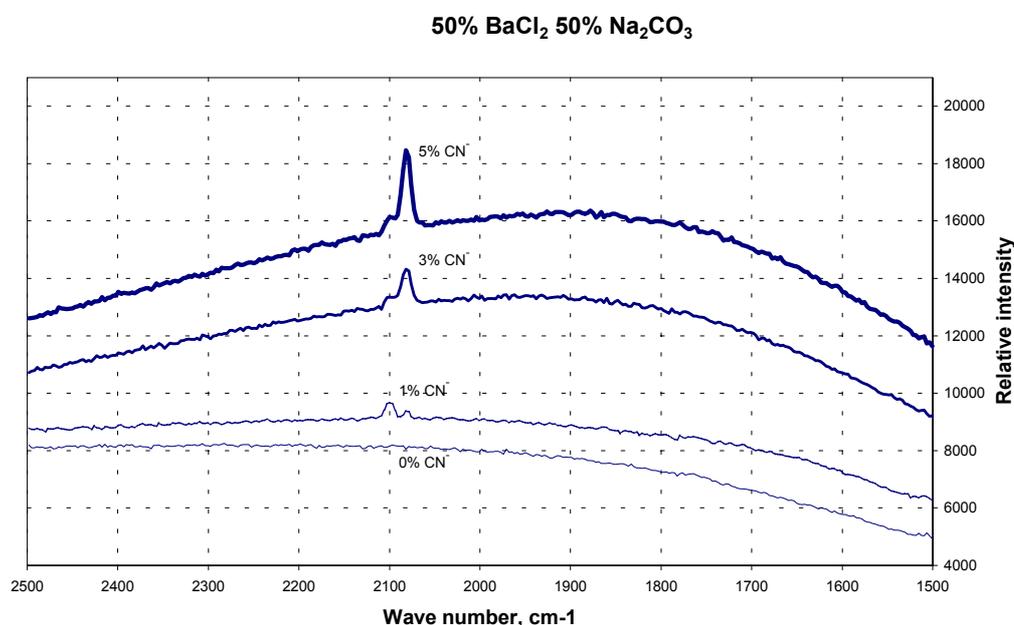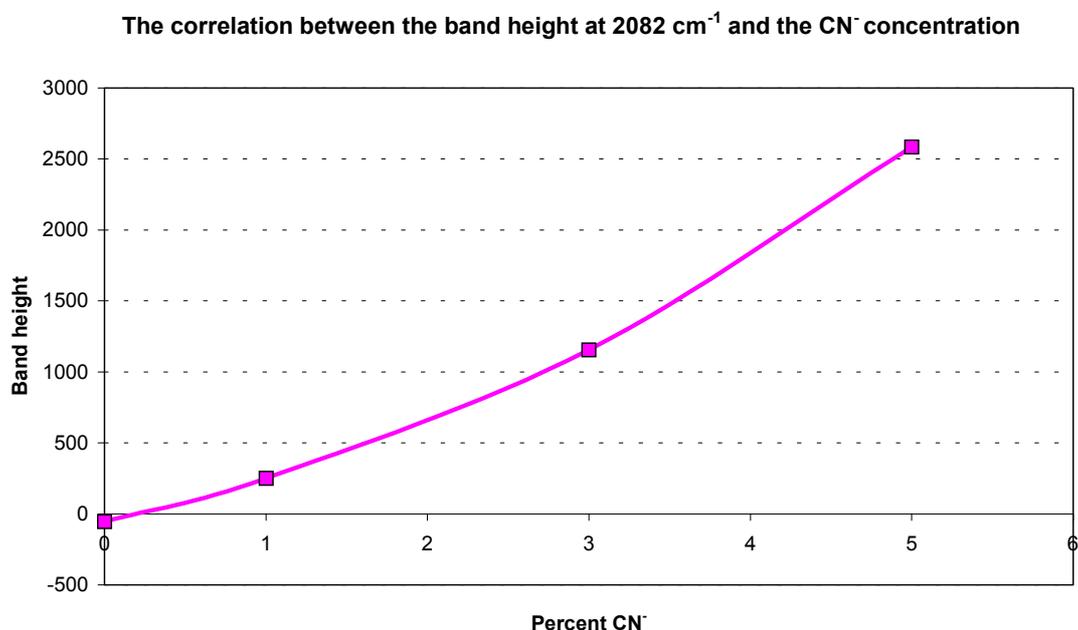
50% BaCl$_2$ 50% Na$_2$CO$_3$

Figure 5: Calibration: Raman spectra of hardened test salt melt mixtures. The concentration of cyanide is shown at each spectrum.

Results and Discussion

The experimental equipment is described in the Experimental section. For

**The correlation between the band height at 2082 cm^{-1} and the CN$^-$ concentration**

calibration purposes four samples were prepared containing 0%, 1%, 3% and 5 % of cyanide, respectively. The measured spectra are shown in Figure 5 and the calibration

Figure 6: The corellation between the band height at 2082 cm^{-1} and the cyanide concentration.

curve is shown in Figure 6.

Another problem had to be addressed: the non-homogeneity of the cooled melt. The usual procedure is to measure Raman spectra at different spots on the crystal surface and to take an average spectrum. A simple experimental procedure, described in the section Experimental above, allowed such repeated measurements to be conducted fast and without refocusing to the crystal surface. The results are shown in Figure 7 and Figure 8. Figure 7 shows nine repetitions of spectra of the same cooled salt melt crystal at different points of the crystal. The non-homogeneity of the cooled melt is evident from peaks that are present in some spectra and absent in others. It can be clearly seen that due to the non-homogeneity of the sample some the spectra are different. However, the average spectrum shows an average composition of the cooled salt melt.

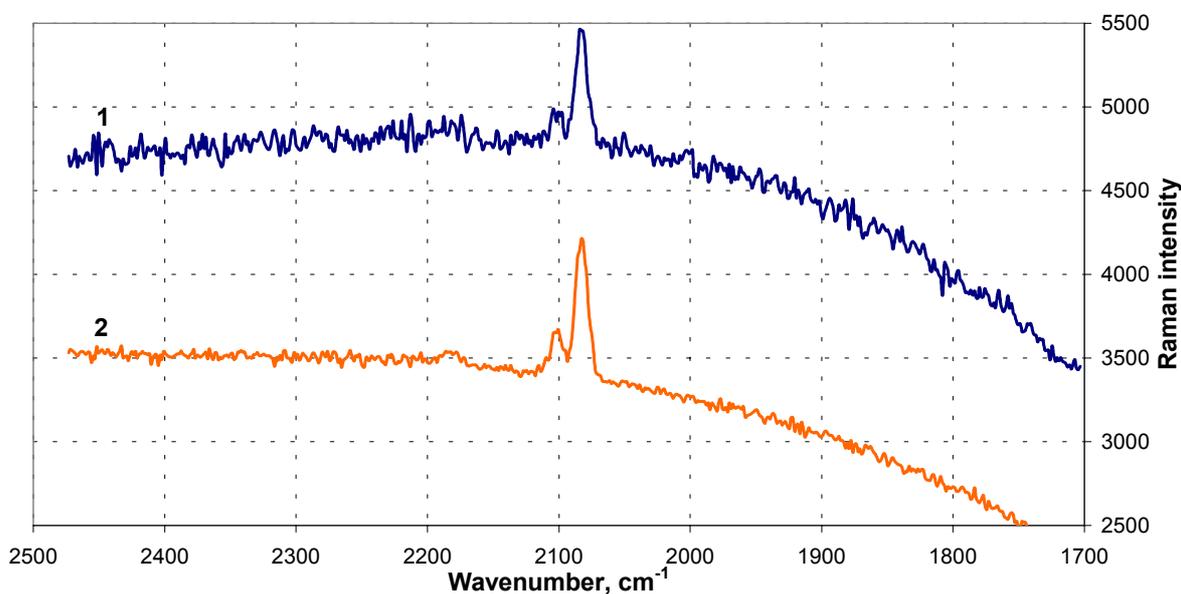Figure 8 shows a comparison of two spectra, depicted with the numbers:
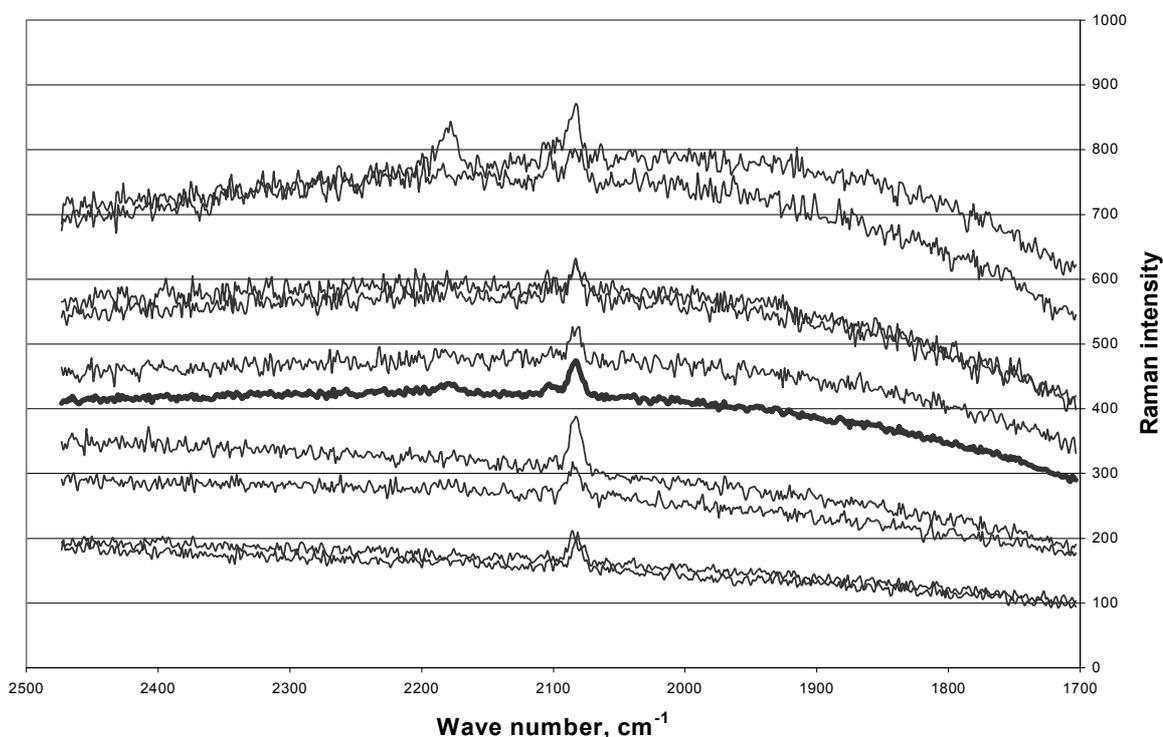
1. the sum of the spectra in Figure 7 (with total scanning time of 9x5=45 seconds) and
2. the spectrum, measured in the same spot for 45 seconds.

Figure 7: Nine spectra measured for 5 seconds each at different spots. The sample on a quartz glass plate was moved planparallely between the exposures. The sample was not moved during the exposure. The spectrum depicted with a bold line is the average spectrum of nine repetitions.

Conclusions

The proposed method for testing the cyanide content in the hot fused salt bath is applicable for industrial use because of a high repeatability, simple measuring equipment maintenance and easy adaptation for automatic sampling and measurement. The drawback of the method is the fact that at non sufficient air intake elemental carbon can be produced which in turn renders the test salt immeasurable due to high

fluorescence. The only way to avoid such instances is to maintain a sufficiently high air

Figure 8: The comparison of two spectra: 1, the sum of nine spectra (each measured for 5 seconds) with a total exposure time of 45 seconds; 2, the spectrum measured in one spot for 45 seconds.

intake rate.

References and Notes

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Povzetek

Prikazan je razvoj postopka za analizo koncentracije cianida v raztaljenih solnih kopelih, ki se uporabljajo za cementiranje jeklenih površin in orodij. Uporabljena je Ramanska spektroskopska metoda, pri čemer je signal speljan preko steklenih vlaken, tako da je občutljiva merilna tehnika lahko v drugem prostoru kot talilne peči. Opisana je tudi možnost popolne avtomatizacije vzorčevanja in izvajanja meritev.