

## Laboratorní a výpočetní technika

### CONDUCTOMETRIC DETERMINATION OF THE OXIDATION OF ORGANIC SUBSTANCES DURING THEIR ELIMINATION FROM CERAMIC PRODUCTS

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Received 8. 3. 1988

*The method for determining the oxidation of organic substances is based on the absorption of carbon dioxide, produced by their combustion, in aqueous solution of barium hydroxide. Formation of an insoluble precipitate of barium carbonate changes the electrical conductivity of the solution, and the effect is utilized for continuous recording of the degree of conversion of the organic substances.*

#### INTRODUCTION

Organic binders are often used in the manufacture of some ceramics to facilitate their forming by pressing, and some special ware is formed by casting in the form of organic suspensions. After the product has been given its final form or following its drying, the organic substances have to be eliminated in the course of firing. Under certain circumstances, the process involved may damage or destroy the final product, and on the other hand the heat liberated during oxidation of the organic substances contributes to fuel economy. To allow the firing of such ware to be conducted as efficiently as possible, one should know the course of the elimination or oxidation of the organic substances present.

The rate of elimination of organic substances depends generally on the conditions of firing, i.e. temperature, composition of the firing atmosphere, the rate and way of its flow in the kiln, etc., and also on the structure of the ware being fired, the content of organic substances, their nature and other factors. In view of the large number of effects influencing the final rate at which the carbonic substances are eliminated, it appears far more useful to determine the rate for the given conditions of firing in the laboratory and to transfer the results obtained in this way to the production scale. A method for laboratory investigation of the elimination of carbonic substances was developed and further modified and subsequently verified on the  $ZrO_2$ -based ceramic system which is formed with the use of various organic binders.

#### THEORETICAL

##### Oxidation of organic substances

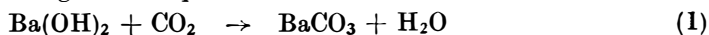
A number of authors have dealt with the course of heterogeneous non-catalyzed reactions between solids and gases [1—3]. A survey of information can be found e.g. in [4]. A method for investigating oxidation of organic substances in a defined atmosphere on the gravimetric principle was earlier employed at the Department of Silicate Technology of the Institute of Chemical Technology at Prague [5]. However, the gravimetric method, advantageous from the standpoint of comparatively easy execution, is unsuitable for some systems. It is particularly the case of a low content of organic substances when the application of the method

is limited by the sensitivity of equipment used to measure the changes in weight, or wherever the oxidation is accompanied by additional processes such as dry distillation of the organic substances involved. The gravimetric method then determines the total loss in weight which, although associated with the amount of organic substances remaining in the ware, does not provide information on the extent of oxidation under the given conditions.

A new method based on conductometric determination of carbon dioxide has been developed to eliminate the drawback mentioned above.

#### Conductometric determination of CO<sub>2</sub>

The method is based on the principle of absorbing the carbon dioxide in an aqueous solution of barium hydroxide with which it reacts producing precipitated barium carbonate according to the equation



Barium carbonate is a poorly soluble substance ( $pK = 8.3$ ). An excess of CO<sub>2</sub> produces barium bicarbonate Ba(HCO<sub>3</sub>)<sub>2</sub> which dissociates in the solution and causes the conductivity to increase [6].

The changes in the concentration of the Ba(OH)<sub>2</sub> solution during reaction (1) can be determined by titration, which is laborious and not much accurate, or continuously using conductometry. This method has a number of advantages: it provides a continuous record of the decreasing concentration of the solution, requires little handling of the toxic barium hydroxide, its execution is simpler and it is easier to protect the solution from coming into contact with the atmosphere containing carbon dioxide. The conductometric determination of CO<sub>2</sub> by means of the barium hydroxide volumetric solution, or that of sodium hydroxide or potassium hydroxide, is described in [7 through 9]. The method has a certain disadvantage of strong temperature dependence of conductivity.

#### EXPERIMENTAL

##### The apparatus employed

A schematic diagram of the experimental arrangement is shown in Fig. 1. The sample is suspended in a silica glass reactor, into which air or an inert gas is supplied from the bottom. The gases can be pre-purified and pre-dried. The reactor is placed in a tubular electric furnace. The gas leaving the reactor passes into the conductometric vessel where it is uniformly dispersed into the Ba(OH)<sub>2</sub> solution through a terminal nozzle consisting of a bundle of capillaries. A glass frit was found to perform unsatisfactorily, as it tended to be readily clogged with the BaCO<sub>3</sub> precipitate. The surface of the reagent solution was covered with an about one centimetre thick layer of kerosene to prevent the solution from reacting with atmospheric CO<sub>2</sub>. In view of the use of capillaries in the bubbler the thickness of the kerosene layer must be greater than the diameter of the escaping bubbles. The temperature of the absorbing solution is kept at a constant level by thermostating the conductometric vessel.

##### Preparation of samples, firing schedule

The oxidation of organic substances was followed on specimens of ZrO<sub>2</sub> stabilized with calcium oxide and formed with an addition of 7 wt. % polyvinyl alcohol (trade name Sloviol), or 1 wt. % of 1 % tylose solution. Using overflow pressing in manual moulds, the mixes were worked into spherical specimens 10 mm in diameter.

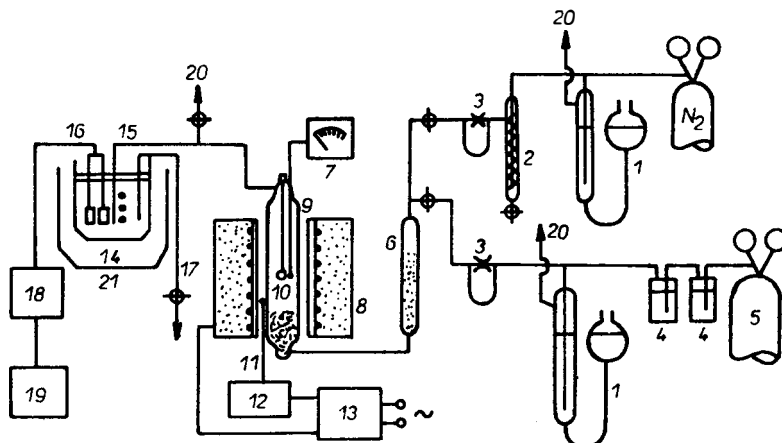


Fig. 1. Schematic diagram of the experimental arrangement;

1 — manostat, 2 — deoxidation column, 3 — flowmeter, 4 — scrubber containing concentrated NaOH solution, 5 — air, 6 — desiccating column, 7 — temperature indicator with Pt-PtRh 10 thermocouple, 8 — tubular furnace, 9 — reactor of silica glass, 10 — specimen, 11 — control thermocouple Pt-PtRh 10, 12 — heating controller, 13 — autotransformer, 14 — conductometric vessel, 15 — capillary bubbler, 16 — electrodes, 17 — drain cock, 18 — conductometer, 19 — potentiometric recorder, 20 — exhaust, 21 — thermostat.

The oxidation was studied during isothermal firing over the range of 400 to 600 °C, either with tempering in nitrogen atmosphere before oxidation, or without this tempering by directly placing the specimen in the heated reactor.

### Measuring method

The conductometric vessel was filled with 0.001 M barium hydroxide solution. The solution was prepared by dissolving  $\text{Ba}(\text{OH})_2$  in boiled distilled water to a concentration of 0.01 M; 25 ml of this solution was pipetted into the conductometric vessel and made up to 250 ml with boiled distilled water. The contents of the vessel was agitated with a magnetic stirrer. Before starting the actual measurement, the solution in the vessel was overlaid with kerosene and saturated until a constant change in conductivity per unit time was achieved. The detecting part of the apparatus was thus ready for measurement. The direct-deflection OK-102/1 instrument by Radelkis, connected to the OH 814 recorder by the same manufacturer, was used to indicate the changes in conductivity.

Following termination of the measurement, the solution should be drained from the conductometric vessel which, including the electrodes, must then be rinsed with distilled water. The electrodes must then be washed with ethanol to remove residual kerosene, then with dilute hydrochloric acid to dissolve the precipitated barium carbonate, and after that with distilled water again.

During the actual measurement the electrodes should be placed at a suitable distance from the bubbling tube and be free of kerosene droplets.

### Evaluation of experimental data

The conductivity data of the absorbing solution obtained during oxidation of the organic substances were used to calculate the concentration ratio  $x$ :

$$x = \frac{c}{c_0} = \frac{\Delta\kappa}{\Delta\kappa_0} \quad (2)$$

where  $c$  is the concentration of carbon dioxide during combustion in the air removing the combustion products,  $c_0$  is the initial concentration of carbon dioxide in the air,  $\Delta\kappa$  is the change in the conductivity of the absorbing solution in the course of the experiment,  $\Delta\kappa_0$  is the initial change in the conductivity of the absorbing solution during the same time interval.

Plotting the absolute value of logarithm  $x$  vs. time according to the equation

$$|\ln x| = k\tau \quad (3)$$

where  $k$  is the rate constant ( $s^{-1}$ ),  $\tau$  is time (s), produced linear relationships whose slope  $k$  was determined. The values obtained are plotted in Fig. 2.

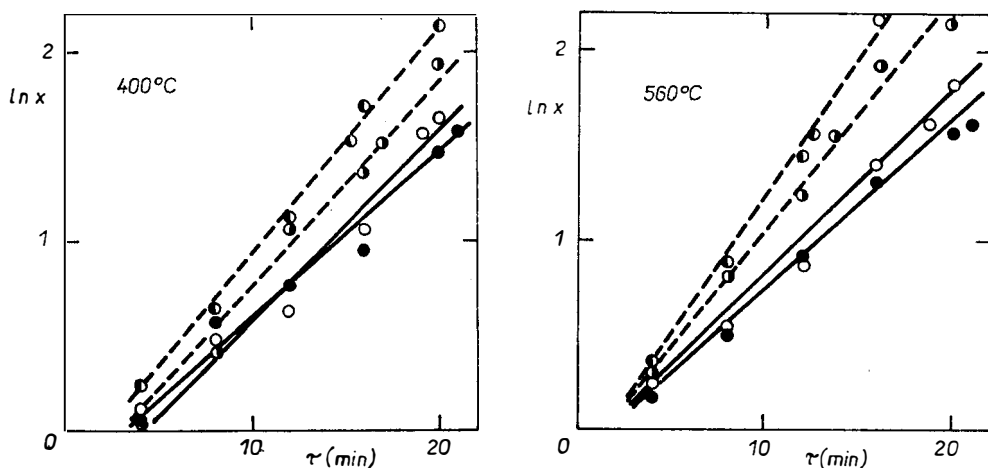


Fig. 2. Time dependence of constant  $K$  (equation (3));  
 ○ — without tempering, tylose; ● — without tempering, PVA; ◐ — with tempering, tylose;  
 ● — with tempering, PVA.

## DISCUSSION

The rate of oxidation of specimens not tempered in nitrogen atmosphere before introducing the flow of air, exhibited virtually no temperature dependence. Over the temperature range studied, the temperature dependence of the chemical kinetics according to Arrhenius's equation is obviously compensated by other effects with an opposite trend, e.g. by structural changes in the ceramic matrix.

The specimens pre-tempered in nitrogen at the required temperature exhibited a temperature dependence of the oxidation rate with a peak at 460 °C. This dependence is probably due to dry distillation of the binder during the tempering of the specimens. The subsequent oxidation is then affected by the amount of these binder removed by distilling as well as by the structural changes in the matrix taking place during this period.

In this case, the oxidation of organic substances can be described by the 1st order kinetic equation

$$c = c_0 \cdot e^{-kt}, \quad (4)$$

where the symbols employed have the designation mentioned above.

## CONCLUSION

Application of the conductometric method in the study of combustion of organic binders in ceramic materials has not so far been published. A similar method was used in study [8] in determining the metabolic respiratory course of plants.

The method employed is selective and capable of recording the amount of carbon dioxide formed, possibly including the carbon monoxide following its oxidation to  $\text{CO}_2$ ; unlike the gravimetric method, it does not detect water which may be liberated during combustion of organic binders. The handling of toxic barium hydroxide is a certain disadvantage; however, this can be substituted with sodium or potassium hydroxide, of course at the expense of sensitivity and the necessity of tempering the solution.

Experimental verification of the conductometric method indicated that for the given  $\text{ZrO}_2$  system, with polyvinyl alcohol or tylose binder, the oxidation represents a process controlled by the 1st order chemical kinetics.

The conductometric determination of the course of burning out can find practical application wherever the gravimetric determination would be distorted by changes in weight not caused by combustion.

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## KONDUKTOMETRICKÉ STANOVENÍ OXIDACE ORGANICKÝCH LÁTEK PŘI JEJICH ODSTRAŇOVÁNÍ Z KERAMICKÝCH VÝROBKŮ

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Průběh odstraňování organických látek z keramických výrobků (např. pojiv nebo plastifikátorů) lze s výhodou sledovat konduktometricky. Tato metoda je založena na jímání vzniklého  $\text{CO}_2$  do vodného roztoku hydroxidu barnatého, kde vzniká sraženina uhličitá barnatého. Tím dochází k poklesu elektrické vodivosti roztoku. Při eventuálním předávkování  $\text{CO}_2$  vzniká hydrogenuhličitá barnatá, čímž vodivost opět vzrůstá.

Schéma použitého zařízení je na obr. 1. Vzorek je umístěn v trubkovém reaktoru, ve kterém lze docílit řízené atmosféry. Reaktor je vyhříván elektrickou pecí. Reakční zplodiny jsou vedeny do konduktometrické nádoby, kde jsou rozptylovány do absorpčního roztoku  $\text{Ba}(\text{OH})_2$ , který je převrstven petrolejem.

Metodika stanovení oxidace uhlikatých látek byla ověřena na vzorku oxidu zirkoničitého, pojeného polyvinylalkoholem, resp. tylosem. Ze získaných dat o vodivosti byl vytvořen poměr koncentrací  $x$  (rovnice 2), kde  $c$  — koncentrace oxidu uhličitého,  $\Delta z$  — změna vodivosti absorpčního roztoku, index 0 značí počáteční hodnotu.

Vynesením logaritmu tohoto poměru oproti času  $\tau$  podle vztahu (3) byly získány lineární závislosti, viz obr. 2, a z nich stanovena hodnota rychlostní konstanty  $k$ .

U vzorků, které před měřením nebyly temperovány v inertní atmosféře, není patrna téměř žádná teplotní závislost této veličiny: u temperovaných vzorků se projevuje maximum při  $460^\circ\text{C}$

То же зřejmě způsobено suchou destilací pojiva, k níž dochází při tepercaci, a dále strukturním změnami při výpalu.

Konduktometrická metoda se ukázala pro sledování oxidace organických látek v keramice jako perspektivní.

Obr. 1. Schéma experimentálního uspořádání;

1 — manostat, 2 — desoxidací kolona, 3 — průtokoměr, 4 — promývačka s koncentrovaným roztokem NaOH, 5 — vzduch, 6 — sušicí kolona, 7 — ukazatel teploty s termočlánkem Pt-PtRh 10, 8 — trubková pec, 9 — reaktor z křemenného skla, 10 — vzorek, 11 — regulační termočlánek Pt-PtRh 10, 12 — regulátor topení, 13 — autotrafo, 14 — konduktometrická nádobka, 15 — kapilárový probublávač, 16 — elektrody, 17 — výpust, 18 — konduktometr, 19 — potenciometrický zapisovač, 20 — odtah, 21 termostat.

Obr. 2. Závislost konstanty  $k$  (rovnice (3)) na čase;

○ — bez tepercace, tylóza; ● — bez tepercace, PVA; ⊙ — s tepercací, tylóza; ⊕ — s tepercací PVA.

## КОНДУКТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ОКСИДАЦИИ ОГРАНИЧЕННЫХ ВЕЩЕСТВ ПРИ ИХ УДАЛЕНИИ ИЗ КЕРАМИЧЕСКИХ ИЗДЕЛИЙ

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Процесс удаления органических веществ из керамических изделий (напр. вяжущих или пластификаторов) можно с преимуществом исследовать кондуктометрически. Данный метод основывается на содирании образующегося  $\text{CO}_2$  в водный раствор гидроксида двухвалентного бария, где образуется осадок карбоната бария. В результате того понижается электропроводность раствора. В случае чрезмерной дозировки  $\text{CO}_2$  образуется гидрокарбонат бария, в результате чего опять повышается проводимость.

Схема применяемой установки находится на рис. 1. Образец помещается в трубчатый реактор, в котором можно получать управляемую атмосферу. Реактор нагревается электрической печью. Продукты реакции направляются в кондуктометрический сосуд, где диспергируют в абсорбционный раствор  $\text{Ba}(\text{OH})_2$ , который покрыт слоем керосина.

Методика определения оксидации углеродистых веществ проверялась на образце оксида четырехвалентного циркония, связанного с поливиниловым спиртом, или тилозой. Из полученных данных относительно проводимости выводили отношение концентраций  $x$  (уравнение 2), где  $c$  — концентрация оксида четырехвалентного углерода,  $\Delta k$  — изменение проводимости абсорбционного раствора, показатель  $\theta$  обозначает исходную величину.

Вынесение логарифма данного отношения на график в сопоставлении с временем согласно отношению (3) получились линейные зависимости (см. рис. 2), из которых, устанавливали величину константы скорости  $k$ .

У образцов, которые до измерения не темперировали в инертной атмосфере, не видна практически никакая температурная зависимость данной величины, у темперированных образцов проявляется максимум при температуре 460 °C. Это очевидно вызвано сухой перегонкой вяжущего, проходящей при темперировании, и далее структурными изменениями при обжиге.

Кондуктометрический метод оказывается при исследовании оксидации органических веществ в керамике весьма перспективным.

Рис. 1. Схема экспериментального упорядочения; 1 — маностат, 2 — десоксидационная колонна, 3 — расходомер, 4 — промывалка с концентрированным раствором NaOH, 5 — воздух, 6 — сушильная колонна, 7 — показатель температуры с термоэлементом Pt—PtRh 10, 8 — трубчатая печь, 9 — реaktor из кварцевого стекла, 10 — образец, 11 — регуляционный термоэлемент Pt—PtRh 10, 12 — регулятор отопления, 13 — автотrafo, 14 — кондуктометрический сосуд, 15 — капиларный барботер, 16 — электроды, 17 — выпускное отверстие, 18 — кондуктометр, 19 — потенциометрический регистратор, 20 — тяга, 21 — термостат.

Рис. 2. Зависимость константы  $K$  (уравнение (3)) от времени; ○ — без темперирования, тилоза, ● — без темперирования, поливинилалкоголь, ⊙ — с темперованием, тилоза, ⊕ — с темперованием, поливинилалкоголь.