

**19TH CTAS ANNUAL
WORKSHOP AND EXHIBITION**

May 12 & 13, 2009

**Chimo Hotel
Ottawa, Ontario, Canada**



CANADIAN THERMAL ANALYSIS SOCIETY

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Tuesday May 12, 2009

Training Session

- 8:00 – 8:30 *Registration*
- 8:30 – 9:30 **TGA-MS and DSC in Materials Chemistry**
S. H. Eichhorn, University of Windsor
- 9:30– 10:15 **What differential scanning and Calvet calorimetry can do for your research**
A. A. Levchenko, Setaram Inc
- 10:15 – 10:45 *Exhibition, Posters & Coffee break*
- 10:45 – 11:30 **Calorimetry is more than just a DSC**
C. A. Potter, TA Instruments, New Castle Delaware, USA
- 11:30 – 12:15 **Thermal Analysis Instrument for Development and Process Optimization**
O. Savard, PerkinElmer LAS Inc.
- 12:15 – 13:15 *Lunch*
- 13:15 – 14:00 **Adiabatic Calorimetry (Accelerating Rate Calorimeters - ARC) and Automatic Pressure Tracking Adiabatic Calorimetry (APTAC)**
P. Ralbovsky, Netzch Instruments Inc
- 14:00 – 14:45 **Measuring the melting point**
T. Basalik and S. Sauerbrunn, Mettler-Toledo Inc.
- 14:45 – 15:15 *Coffee break*



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Vendor Presentations

- | | |
|---------------|---------------------------------|
| 15:15 – 15:35 | TA Instruments |
| 15:35 – 15:55 | Mettler-Toledo Inc. |
| 15:55 – 16:15 | Setaram Inc |
| 16:15 – 16:35 | PerkinElmer LAS Inc |
| 16:35 – 16:55 | Netzsch Instruments Inc. |

Social Event:

Reception, Exhibition and Poster Presentation

17:00 – 18:30



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Wednesday May 13, 2009

Technical Session

- 08:00 – 08:30 *Registration*
- 08:30 – 09:15 **Plenary Lecture**
Thermal analysis of metal nanoparticles (MNPs) protected by organic (mono)layers
S. H. Eichhorn, University of Windsor
- 09:15 – 09:30 **Open Forum**
Moderator: S. H. Eichhorn, University of Windsor
- 09:30 – 09:50 **Measuring the heat of evaporation by TGA/DSC**
T. Basalik and S. Sauerbrunn; Mettler-Toledo Inc.
- 09:50 – 10:10 **Thermodynamic modeling of hematite (Fe₂O₃) solubility at elevated temperature**
S. C. Mojudar, M. Reird and V. G. Papangelakis; Department of Chemical Engineering and Applied Chemistry, University of Toronto
- 10:10 – 10:40 *Exhibition, Posters & Coffee break*
- 10:40 – 11:00 **Part I: Amorphous Content of Crystalline Materials by Differential Scanning Calorimetry**
C. Potter and S. Hunt; TA Instruments, Delaware USA and Ontario Canada
- 11:00 – 11:20 **Part II: Amorphous Content of Crystalline Materials by Dynamic Vapor Sorption and Microcalorimetry**
C. Potter and S. Hunt, TA Instruments, Delaware USA and Ontario Canada



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- 11:20 – 11:40 **Thermoporometry: a useful tool to study the fundamental properties of confined water in porous media**
Y. Maham, T. M. Kuznicki and S. M. Kuznicki; Department of Chemical and Materials Engineering, University of Alberta
- 11:40 – 12:00 ***Annual General Meeting.***
- 12:00 – 13:00 *Lunch*
- 13:00 – 13:20 **Urea nitrate decomposition using thermal methods**
S. Singh, H. Feng, K. Armstrong, and R. Turcotte; Canadian Explosives Research Laboratory, Natural Resources Canada
- 13:20 – 13:40 **Analysis of pharmaceutical polymorphs by fast heating rate DSC**
T. Basalik; Mettler-Toledo Inc.
- 13:40 – 14:00 **Reaction enthalpy during high temperature aqueous oxidation of pyrite, pentlandite and chalcopyrite**
S. C. Mojumdar¹, I. Bylina¹, L. Trvani², P. Tremaine² and V. G. Papangelakis¹; ¹Department of Chemical Engineering and Applied Chemistry, University of Toronto; ²Chemistry Department, University of Guelph
- 14:00 – 14:30 *Exhibition, Posters & Coffee break*
- 14:30 – 14:50 **Taking advantage of thermal analysis in aluminum recycling**
M. Mahfoud¹ and D. Emadi²; ¹Departement of Mechanical Engineering, College of the North Atlantic-Qatar, Doha, Qatar; ²CANMET-Energy, Natural Resources Canada



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- 14:50 – 15:10 **The use of calorimetry for studying cement/cementitious material and chemical admixtures interactions**
P. C. Nkinamubanzi; Institute for Research in Construction, National Research Council Canada
- 15:10 – 15:30 **Determining critical properties for nanocrystalline silver antimicrobial activity via heat treatment: a kinetic study**
P. L. Nadworny^{1,2}, B. K. Landry¹, O. Omotoso³, Y. Maham¹, J. C. Burrell¹, and R. E. Burrell.^{1,2}
¹Department of Chemical and Materials Engineering,
²Department of Biomedical Engineering, University of Alberta,
³Natural Resources Canada, CANMETENERGY, Alberta
- 15:30 – 16:00 *Exhibition, Posters & Coffee break*
- 16:00 – 16:20 **Coordination and inclusion compounds formed between a metal (II) dibenzoylmetanate (Co, Ni, Zn, Cd) and quinoline or isoquinoline: thermal stability and dissociation mode**
E. B. Okeke and D. V. Soldatov
Department of Chemistry, University of Guelph
- 16:20 – 16:40 **Ammonium nitrate emulsion: physical properties and decomposition using thermal methods**
S. Goldthorp, H. Feng, S. Singh and R. Turcotte
Canadian Explosives Research Laboratory, Natural Resources Canada
- 16:40 – 17:00 **Thermal hazard assessment of nitrobenzene /dinitrobenzene mixtures**
C. Johnson¹, C. Badeen¹, R. Turcotte¹, E. Hobenshield², and S. Berretta²
¹Canadian Explosives Research Laboratory, Natural Resources Canada
²NORAM Engineering Constructors Ltd, Vancouver, BC



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Poster Session

Characterization of thermal properties of FOX-7: A multifaceted thermal analyses

B. Acheson S. Singh and D. E. Jones

Canadian Explosives Research Laboratory, Natural Resources Canada

Use of calorimetric techniques for the determination of energetics, thermodynamics and kinetics of hydrogen storage in various materials

P. Le Parlouer¹, C. Mathonat¹, N. Garcia²

¹Setaram Instrumentation, Caluire, France; ²Setaram Inc., Newark, USA

Controlled Humidity Dynamic Mechanical Analysis

Charles Potter, TA Instruments, New Castle Delaware USA

Effect of zinc(II) doping on thermal and optical properties of potassium hydrogen phthalate (KHP) crystals

S. Parthiban¹ S. Murali¹ G. Madhurambal² S. P. Meenakshisundaram¹ and S. C. Mojumdar³

¹Department of Chemistry, Annamalai University, Annamalainagar, India

²Department of Chemistry, A.D.M. College for Women, Nagapattinam, Tamil Nadu India

³Department of Chemical Engineering and Applied Chemistry, University of Toronto

Os(VIII)- Doping effects on the properties and crystalline perfection of potassium hydrogen phthalate (KHP) crystals

K. Muthu¹, G. Bhagavannarayana² C. Chandrasekaran, S. Parthiban¹, S. P. Meenakshisundaram¹ and S. C. Mojumdar³

¹Department of Chemistry, Annamalai University, Annamalainagar, India.

²Materials Characterization Division, National Physical Laboratory, New Delhi, India.

³Department of Chemical Engineering and Applied Chemistry, University of Toronto

Effect of storage time on the oxidation enthalpy of pyrite

S. C. Mojumdar, I. Bylina, V. G. Papangelakis

Department of Chemical Engineering and Applied Chemistry, University of Toronto



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Influence of Mg on hematite solubility in sulfuric acid solutions at elevated temperature

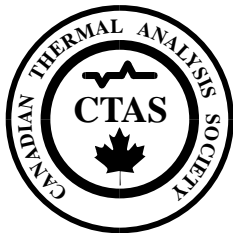
S. C. Mojumdar, M. Reird and V. G. Papangelakis; Department of Chemical Engineering and Applied Chemistry, University of Toronto

Thermal and porosimetric analysis used for microstructure characterization of metakaolin sand blended Portland cement mortar

Ľ. Krajčí¹, S. C. Mojumdar², M. Kuliffayová¹ and I. Janotka³

¹*Institute of Construction and Architecture of Slovak Academy of Sciences, Slovak Republic,* ²*University of Toronto, Department of Chemical Engineering and Applied Chemistry,* ³*Building Testing and Research Institute, Slovak Republic*

ABSTRACTS



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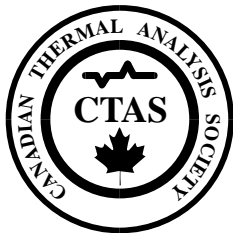
TGA-MS and DSC in Materials Chemistry

S. H. Eichhorn
University of Windsor

Presented will be applications of Differential Scanning Calorimetry (DSC), Thermal Gravimetric Analysis (TGA), and TGA coupled with Mass Spectrometry in materials chemistry and engineering. Examples for DSC will include the characterization of phase transitions in liquid crystals and other mesophases as well as in nanoparticles. Examples for TGA and TGA-MS will include the determination of thermal stability, the solvent content of crystalline and (meso)porous materials, and the compositions of nanoparticles and functionalized carbon nanotubes. DSC and TGA-MS are often complemented by several other characterization techniques. Emphasis will be placed on examples that require other characterization techniques for a meaningful and comprehensive interpretation of the obtained DSC and TGA-MS results.

Biography

S. Holger Eichhorn obtained his diploma in chemistry from the University of Bremen (Germany) in 1991 and finished his PhD in 1995. He did his PhD work on the (photo)polymerization of dyes mainly at the University of Bremen and at the Humboldt University in Berlin. He became an expert in the synthesis and characterization of liquid crystals during his postdoctoral stays with Duncan W. Bruce (University of Exeter, England, 1996-7), Neville Boden / Richard J. Bushby (University of Leeds, England, 1997-8) and Timothy M. Swager (MIT, USA, 1999-2001). Eichhorn started his independent career as materials chemist at the University of Windsor in 2001. His group presently develops aromatic self-organizing compounds for organic electronics and metal nanoparticles for inorganic-organic hybrid materials. These projects have been funded by governmental (NSERC, CFI, OIT, and OCE) and industrial partners (Xerox, Exxon Mobil, Dofasco, and Barrick Gold).



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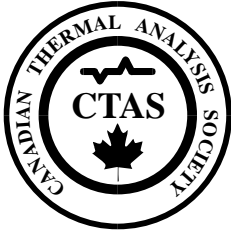
What differential scanning and Calvet calorimetry can do for your research?

A. A. Levchenko
Setaram Inc., Newark, California, U.S.A.

Twinned Calvet calorimeters have been known for decades since their introduction by Edouard Calvet in 1948, yet recent developments in engineering and manufacturing have opened the door to new applications including calorimetry under extreme conditions. These new applications take advantage of not only unprecedented baseline stability and sensitivity of the Calvet calorimeters but also an inherent compensation mechanism of the twin design permitting to measure heat transfer with high accuracy. This presentation covers theoretical and practical aspects of Calvet calorimetry. New and published data will be presented to illustrate capabilities and advantages of the Calvet calorimeters.

Biography

Dr. Andre Levchenko is an expert in thermal analysis and calorimetry of organic-inorganic composites, inorganic materials, and nanophases. He finished his PhD in condensed matter physics in 2002 studying phase transition in liquid crystalline polymers at the Russian Academy of Sciences. Before joining Setaram Inc. Dr. Levchenko was a researcher in the Peter A. Rock Thermochemistry Laboratory led by Prof. Alexandra Navrotsky (University of California at Davis). The Peter A. Rock Thermochemistry Laboratory is renowned worldwide for its unique custom-build high temperature calorimeters and cutting edge research in thermochemistry of high temperature materials. He was a visiting scholar at Max-Planck Institute for Polymer Research in Mainz and Dresden (Germany) and University of California - Davis while studying for his PhD thesis. He has also a background in other techniques complementary to thermal analysis including X-ray diffraction, several spectroscopic techniques, neutron scattering, as well as, gas sorption. He has published more than 20 papers in peer-reviewed journals.



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Calorimetry is more than just a DSC

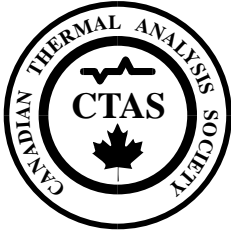
C.A..Potter

TA Instruments, New Castle Delaware, USA

Differential Scanning Calorimetry (DSC) has wide industrial applications for polymers, pharmaceuticals, and many other commercial materials. But DSC is only one of many different types of calorimeters. Calorimeters are classified by their mode of measurement, the sample size, sample type, and many other ways. All calorimeters measure heat, but proper selection of the calorimeter will greatly facilitate the ease of measurement and the quality of the resulting data. Besides DSC, what are the other common calorimeters and how are they used?

Biography

Dr. C. Potter obtained his PhD in analytical chemistry from the university of Connecticut. Since then he has worked in diverse research environments in thermal analysis and hazard analysis. He is currently a senior application scientist at TA Instruments, helping customers with TA problem solving.



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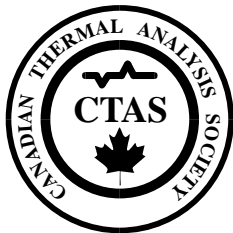
Thermal Analysis Instrument for Development and Process Optimization

O. Savard
PerkinElmer LAS Inc.

In this word of constant evolution, industries and researchers need the best tool available to develop and understand their material. To do so, they need all the flexibility and performance available to study materials under controlled environment that will reproduce real life uses and manufacturing process. Since each material is different, different techniques have to be used to fully understand them. This presentation will focus on two majors industries where thermal analysis could play an important role in making their products better: pharmaceutical and polymer. Although, many standard thermal analysis technique are still really useful (e.g. DSC, TGA, etc.), new ways to analyse material will provide answers that were not available before. This presentation will focus on some of these innovative techniques such as: HyperDSC™, UV-DSC, Raman-DSC, TGA-IR and DMA (curing, %RH and immersion

Biography

Olivier received his M.Sc. from Simon Fraser University (Burnaby, BC) in 2006 in the field of polymer chemistry after completing his B.Sc. in chemistry at Université Laval (Québec City). He then worked for a fuel cell company, as a research scientist, before joining PerkinElmer Canada in June 2007 as a product specialist for the material characterization product line (molecular and thermal analysis). In that role, his assignment is to provide technical training and support to PerkinElmer sales engineers, service engineers and customers in the related fields of thermal analysis (DSC, DMA, TGA, STA) and molecular spectroscopy (FTIR, UV/Vis, Microscopy, Imaging, Raman Spectroscopy) products throughout Canada.



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Adiabatic Calorimetry (Accelerating Rate Calorimeters - ARC) and Automatic Pressure Tracking Adiabatic Calorimetry (APTAC)

P. Ralbovsky
Netzsch Instruments, Inc.

This deals with applications for the study of thermal hazards, energetic materials and the development of safe batteries. The topics of discussion will be:

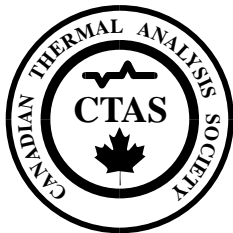
- Adiabatic Calorimetry Overview
- Pressure and non-pressure balancing systems
- Energetic Material Application
- Process Safety/Thermal Hazards Application
- Battery Safety & Development Application

Accelerating Rate Calorimeters (ARC) and Automatic Pressure Tracking Adiabatic Calorimeters (APTAC). Adiabatic reaction calorimeters help industry to operate safely and profitably. As highly versatile, miniature chemical reactors, they measure thermal and pressure properties of exothermic chemical reactions. The resulting information helps engineers and scientists identify potential hazards and address key elements of process safety design including emergency relief systems, effluent handling, process optimization, and thermal stability. Industries, such as chemicals, pharmaceuticals, and energy, as well as the government agencies and laboratories use adiabatic reaction calorimeters to study chemical kinetics, storage and transportation issues, process interruptions, and chemical process design. Adiabatic reaction calorimeters are also used to investigate accidents and develop air bags, rechargeable batteries, spacecraft and rocket propulsion.

Biography

Mr. Ralbovsky recently started working as a calorimetry expert for Netzsch Instruments in 2009. Working for Arthur D. Little, Inc. and TIAX LLC, Mr. Ralbovsky has been conducting thermal and calorimetry measurements for the past 20 years. He has developed new calorimeters, methodologies and other analytical instruments for industry, NASA and the military. He won numerous awards for his work including Arthur D. Little's highest award, The Ketteringham Prize, as well as international instrument design competitions.

Mr. Ralbovsky earned his BS Physics at Union College in Schenectady, NY. He is an active member of AIChE, ASTM, NATAS, and The Reactivity Management Roundtable. He has written numerous papers and articles concerning Battery Safety, Adiabatic Calorimetry, Thermal Hazards Screening, and Runaway Reactions.



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Measuring the Melting Point

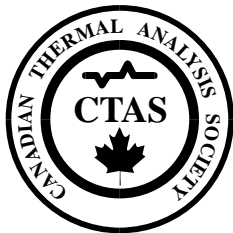
T. Basalik and S. Sauerbrunn
Mettler-Toledo Inc., Columbus, OH

The melting point (or melting range) is the most often measured thermal transition of materials. It is used to qualitatively identify an unknown material. It can determine the purity of fine organic compounds. It is even used to determine the type of alloy of a metal sample. This tutorial will include a broad range of analysis techniques that are used to analyze the melting point of many different kinds of samples.

Biography

Tom Basalik is the Technical Support Manager for the Material Characterization group of METTLER TOLEDO. He has a BS in Chemical Engineering from Drexel University and a MBA from Loyola of Chicago.

Tom has been involved in reaction calorimetry and thermal analysis with METTLER TOLEDO for the past 19 yrs. Prior to his current employment he spent time with the Foxboro Company developing process analytical instrumentation and with other organizations in the polymer and pharmaceutical industries.



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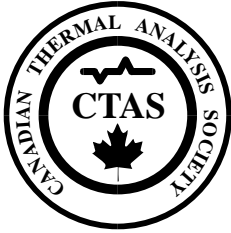
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Thermal analysis of Metal NanoParticles (MNPs) protected by organic (mono)layers

S. H. Eichhorn
University of Windsor

Especially thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) have become important techniques in the characterization of MNPs. TGA analysis is one of the few characterization techniques that provide information on both the metal core and the attached organic ligands by determining the mass ratio of organic material to metal core. Examples will describe how these mass ratios afford the calculation of packing densities of organic ligands on the surface of MNPs when combined with transmission electron microscopy and/or X-ray diffraction. Other examples will outline the less common application of TGA and TGA-MS for determining contents of different ligands as well as inorganic and organic impurities. DSC analysis has been conducted mainly on partially crystalline MNPs to obtain melting temperatures and enthalpies. In specific cases, however, DSC may also provide quantitative information on the thermal stability of the organic layer attached to MNPs. Finally, the recent applications of Isothermal Titration Calorimetry (ITC) to the investigation of growth, aggregation and binding of MNPs will be presented.



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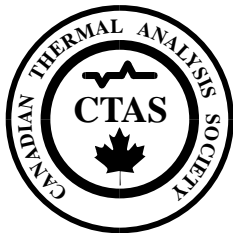
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Measuring the Heat of Evaporation by TGA/DSC

T. Basalik and S. Sauerbrunn
Mettler-Toledo, Inc. Columbus, OH

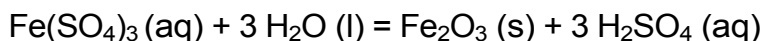
Heat of evaporation is the amount of heat required to make a physical change from the liquid phase to the gas phase. This heat is required for the proper design of any industrial process where a liquid needs to be evaporated such as: water treatment plants, chemical distillations and drying operations. This heat cannot be measure with a DSC alone because the sample changes weight as the phase transition proceeds. This heat cannot be measured by TGA alone because it does not measure the heat flow into the sample. The TGA/DSC1, however, measure both the rate of weight loss and the rate of heat flow during the entire evaporation process. Data presented will demonstrate the measurement of the heat of evaporation for several materials using the TGA/DSC1 instrument.



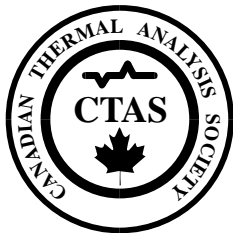
Thermodynamic modeling of hematite (Fe₂O₃) solubility at elevated temperature

S. C. Mojumdar, M. Reid and V. G. Papangelakis
Department of Chemical Engineering and Applied Chemistry
University of Toronto, Toronto, Ontario, Canada

Development of models for electrolyte systems is an important subject of research in applied thermodynamics because of the considerable role that electrolytes play in separation processes, environmental applications, production of energy sources, electrochemical processes, hydrometallurgy and other applications. Chemical models are very useful when they can accurately describe the behavior of electrolyte solutions over wide ranges of temperature, pressure and concentration, and predict solution properties up to saturation levels. Obviously, models need to be validated against experimental measurements before they can be considered trustworthy and reliable. Nevertheless, once a reasonable degree of confidence is built, they can prove themselves extremely powerful. Then, they can describe and validate available laboratory or pilot scale data and predict with confidence beyond the range of available data even more complex systems. Hydrometallurgical processes at elevated temperatures are receiving more attention recently due to new materials of construction, faster kinetics, selectivity against iron and stability of produced residues. Iron is present as a major impurity in all hydrometallurgical processes. A major advantage of high-temperature hydrometallurgical processes, in particular, is that iron precipitates in-situ as hematite during autoclave leaching. The hydrolytic precipitation of Fe(III) as hematite, as compared to other iron phases, from sulphate solutions is advantageous because it regenerates the maximum amount of acid to be used in-situ in the leach process (such as in the laterite PAL process):



A comparison of our modeling results with experimental results of hematite solubility in 10 to 70 g/L H₂SO₄ solutions at 130 to 270°C has proved that the current OLI data base is good for hematite solubility modeling.



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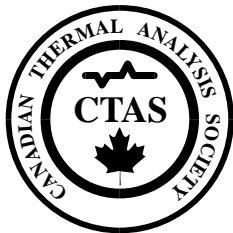
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Part I: Amorphous Content of Crystalline Materials by Differential Scanning Calorimetry

C. Potter and S. Hunt

TA Instruments, Delaware USA and Ontario Canada

The amorphous content will affect the physical properties and stability of a crystalline material such as a pharmaceutical, confection, or semicrystalline polymer. Many techniques are used to detect and quantitate amorphous content with differential scanning calorimetry (DSC), dynamic vapor sorption analysis, and microcalorimetry being the techniques of choice for amorphous content quantitation. DSC, modulated DSC, rapid heating DSC, and large sample DSC techniques will be presented.



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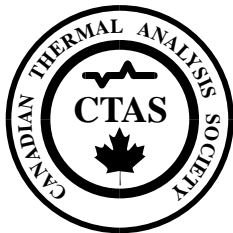
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Part II: Amorphous Content of Crystalline Materials by Dynamic Vapor Sorption and Microcalorimetry

C. Potter and S. Hunt

TA Instruments, Delaware USA and Ontario Canada

In addition to differential scanning calorimetry, gravimetric dynamic vapor sorption (DVS) analysis, vapor sorption microcalorimetry, and solution calorimetry are also used to quantify amorphous content in crystalline materials. Humidity adsorption isotherms, humidity ramp, and humidity jump DVS methods are all used for amorphous content determination, and in a similar manner, calorimetric humidity adsorption techniques are also used. In addition, solution calorimetry is used to determine amorphous by comparison of the heat of solution of a sample to the heats for a completely amorphous and completely crystalline reference.

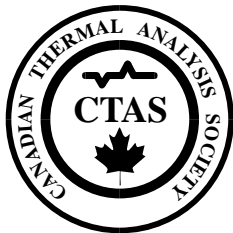


Thermoporometry: A useful tool to study the fundamental properties of confined water in porous media

Y. Maham, T. M. Kuznicki and S. M. Kuznicki
Department of Chemical & Materials Engineering
University of Alberta, Edmonton, AB, Canada

The texture of porous materials with different pore sizes can be characterized by a calorimetric study of the liquid-solid state transition in a capillary condensation process. This method is called thermoporometry, which is based on the thermodynamic conditions of liquid-solid equilibrium inside the porous materials. This method is applied to rigid pores such as zeolites, polymers, or flexible pores, such gels, membranes and biological systems. We have chosen zeolite samples with different pore sizes for this study. The pore sizes of these samples were modified by Ba, Ca, Sr, Na, and Li ion exchange to change their pore diameters.

These zeolite samples were saturated by distilled water to ensure that all the pores were filled with water and there is also extra bulk water in the DSC cells. Two melting points were measured the confined and bulk water melting points. The melting point of confined water is a function of the pore size of the porous media while bulk water is always at 273.15K. We were able to obtain the thermodynamic properties of the confined water such as heat of melting in nano-scales. The results obtained by this technique are compatible with other techniques such as ^1H NMR spectroscopy, XRD, and others. The theoretical basis and also the limitation of this technique will be discussed.

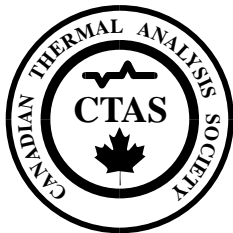


Urea nitrate decomposition using thermal methods

S. Singh, H. Feng, K. Armstrong, R. Turcotte
Canadian Explosives Research Laboratory
Natural Resources Canada, Ottawa, Ontario, Canada

Urea ($\text{O}=\text{C}(\text{NH}_2)_2$) is readily available as an inexpensive nitrogen source in fertilizers and a stabilizer in emulsion explosive formulations. Solutions of urea are basic and when these solutions are neutralized with nitric acid, urea nitrate (UN) is formed. This product is capable of being used in improvised explosives. As such, it has been identified in various terrorist incidents such as the first World Trade Centre bombing in New York city in 1993. Work at the Canadian Explosives Research Laboratory is underway to better understand the thermal stability of UN. Surprisingly few direct comparisons of UN thermograms are available in the open literature, and many of these reports date from the era when temperature difference measurements (DTA) were largely in use.

We present the thermal decomposition behaviour of UN under non-isothermal conditions using a variety of techniques; DTA, differential scanning calorimetry (DSC), simultaneous thermogravimetry-calorimetry-infrared spectroscopy-mass spectroscopy (TG-DSC-FTIR-MS) and accelerating rate calorimetry (ARC). Decomposition is exothermic under confined conditions, and endothermic when unconfined. Upon scaling up the sample size, under closed and adiabatic conditions, the expected decrease in thermal decomposition temperature is observed. Using TG-DSC-FTIR-MS, the first mass loss is coincident with the first detected endotherm. Ammonia and nitric acid are evolved, and suggests a decomposition pathway similar to ammonium nitrate in which the nitrate salt first dissociates to its component acidic and basic adducts.



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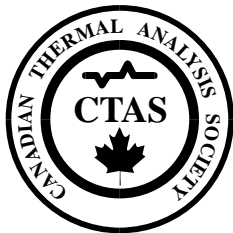
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Analysis of Pharmaceutical Polymorphs by Fast Heating Rate DSC

T. Basalik, B. Greil and S. Sauerbrunn
Mettler-Toledo, Inc., Columbus, USA

Pharmaceutically active compounds have many different functional groups such as: -OH, -COOH, -NH₂, etc. These chemical groups give the compound its activity (or reactivity) in the treatment of medical symptoms and diseases. These same chemical groups may cause the molecule to form different crystalline unit cells. These different crystal forms are called polymorphs. Each of the polymorphic forms might have its own dissolution rate and/or pharmacological activity. It is important to determine the polymorphic form of compound for both patent rights and the ultimate effectiveness in treating the medical condition.

This paper will demonstrate how to use high heating rate DSC experiments to elucidate the different polymorphic states of a compound using the Mettler DSC 823^e. The phenylbutazone will be analyzed to show the utility of this technique.



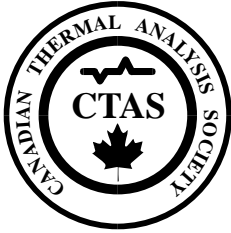
Reaction enthalpy during high temperature aqueous oxidation of pyrite, pentlandite and chalcopyrite

S. C. Mojumdar¹, I. Bylina¹, L. Trvani², P. Tremaine² and V. G. Papangelakis¹;

¹Department of Chemical Engineering and Applied Chemistry, University of Toronto;

²Chemistry Department, University of Guelph

Pressure Oxidation is an industrial process that involves oxidation of sulphide minerals with oxygen in aqueous solution at high temperature in pressure vessels to recover metal values. Because of the high exothermicity, autothermal operation of pressure oxidation reactors is very desirable for energy efficiency and utilisation. Consequently, the measurement, or calculation of the Pressure Oxidation reaction enthalpy is crucial in the design of such operations. Even if enthalpies can be estimated from standard thermochemical data, these values can only be used as an approximation of the actual process heat requirements. We have used a heat flow differential scanning calorimeter (DSC C80) from Setaram designed for measurement of heat of mixing and heat of reaction at normal and high temperatures and pressures in this work. A calorimetric method for determining the enthalpy of the aqueous oxidation of sulfide minerals at high temperatures and oxygen pressures has been developed and evaluated under conditions relevant to industrial pressure oxidation operations. This information is important for heat balance calculation and optimization of the pressure reactor design. Enthalpy measured during oxidative dissolution of pyrite (Valdenegrillos, Spain), pentlandite with pyrrhotite (Sudbury, Ontario, Canada) and chalcopyrite (Victoria, Australia) minerals at 150 °C and partial oxygen pressures of 3.4 and 5.5 MPa have been performed and found to be consistent with theoretical expectations.



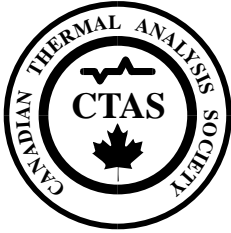
Taking advantage of thermal analysis in aluminum recycling

M. Mahfoud¹ and D. Emadi²

¹Departement of Mechanical Engineering, College of the North Atlantic-Qatar, Doha, Qatar; ²CANMET-Energy, Natural Resources Canada

There has been a significant growth in the aluminum usage in the recent years due to the development of new alloys and new applications. Most aluminum alloys in commercial use today were developed primarily based upon the elemental alloying additions needed to achieve the target performance requirements, including such properties as strength, toughness, and/or corrosion resistance. However, most of the aluminum alloys are mainly being prepared by the addition of alloying elements to primary aluminum without considering the use of secondary alloys. Considering the environmental impact of producing aluminum alloys and availability of scrap aluminum, the recycling of aluminum is becoming very attractive.

In today's market, most scrap aluminum from different sectors (automotive, aerospace, etc) end up being mixed once in the scrap yard. Most current recycling industries are not equipped with shredding, sorting and separation technologies due to their high cost, and as a result different alloys are mixed and some of the alloying elements become trace/tramp elements in the recycled alloy. Therefore, the understanding of the effects of these trace elements on the mechanical properties is of vital importance. This research work aims at understanding the effects of these elements on the solidification characteristics of the alloys using thermal analysis techniques. The present paper presents the principles of the computer-aided cooling curve analysis (CA-CCA) and its application in determining the effect of trace elements on the formation of different phases at different stages of the solidification process.



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The use of calorimetry for studying cement/cementitious material and chemical admixtures interactions

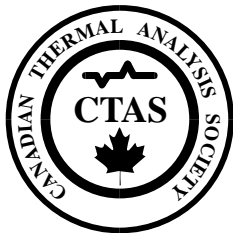
P. C. Nkinamubanzi

Institute for Research in Construction

National Research Council Canada, Ottawa, Ontario, Canada

Calorimetry is a useful tool to study the hydration reaction of cement and its interactions with various chemical and mineral admixtures.

A semi-adiabatic calorimetric method was developed and used to study the reactivity of cements from various sources and the effect of mineral and chemical admixtures on the hydration of the cement pastes. The decreasing of the integral heat developed due to the presence of supplementary cementing material was illustrated by this technique. The effect of accelerator admixtures on the rate of hydration of the cement pastes was also studied by this technique. Simultaneous measurements of the heat developed and the conductivity of the cement pastes were also studied in this work. Both techniques used simultaneously give good information on the interactions between cement/cementitious materials and chemical admixtures.



Determining critical properties for nanocrystalline silver antimicrobial activity via heat treatment: a kinetic study

P. L. Nadworny^{1,2}, B. K. Landry¹, O. Omotoso³, Y. Maham¹, J. C. Burrell¹, and R. E. Burrell.^{1,2}

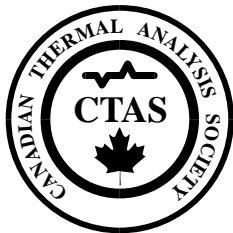
¹Department of Chemical and Materials Engineering, ²Department of Biomedical Engineering, University of Alberta, ³Natural Resources Canada, CANMETENERGY, Alberta

The mechanisms of action (MOA) of nanocrystalline silver wound dressing antimicrobial activity are not understood. Previous studies have shown that dressing properties change with 24 hour heat treatments above 75°C. This study examined the kinetics of heat treatment to establish critical properties for dressing activity that are important to our understanding of nanocrystalline silver dressing production, storage and MOAs.

Dressings were heat-treated at 90, 100 and 110°C from 2 to 50 hours and analyzed using log reductions, zones of inhibition, atomic absorption spectroscopy (AAS), scanning electron microscopy (SEM), x-ray diffraction (XRD), and x-ray photoelectron spectroscopy (XPS). Heat flow during heat treatments was measured by differential scanning calorimetry (DSC).

At 100°C, a change in heat flow at ~7 hours corresponded to decreased bacteriostatic longevity and increased crystallite size. From 17.5 to 22 hours, after a critical crystallite size (~30 nm) was reached, a second change in heat flow occurred, corresponding to decreased bactericidal efficacy and a rapid grain growth. At 90°C, an initial change in heat flow occurred at 15 hours with corresponding physical/biological changes. Decreases in bactericidal efficacy, soluble silver, and oxygen were not apparent within 24 hours. At 24 hours, the critical crystallite size was reached, and the second change in heat flow occurred from 24 to 32 hours. With 110°C heat treatments, changes in dressing properties occurred before a stable DSC baseline was obtained, preventing measurement of heat flows associated with these changes. The grain growth exponent was 2.8 for 100-110°C, with an activation energy of 177 kJ/mol.

Overall, properties related to the nanostructure of the dressings are critical for biological activity, and should be taken into consideration for the development of future nanocrystalline silver products.



Coordination and inclusion compounds formed between a metal (II) dibenzoylmetanate (Co, Ni, Zn, Cd) and quinoline or isoquinoline: thermal stability and dissociation mode

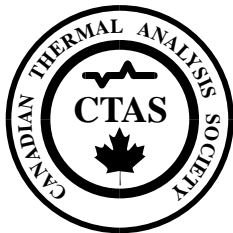
E. B. Okeke and D. V. Soldatov

Department of Chemistry

University of Guelph, Guelph, Ontario, Canada

The addition of either quinoline (Q) or isoquinoline (Iq) to metal dibenzoylmetanates $M(\text{DBM})_2$ (DBM is PhCOCHCOPh^-) yielded three series of crystalline products: (1) $[M(\text{DBM})_2\text{Q}_2]$, $M = \text{Co, Ni, Zn, Cd}$; (2) $[M(\text{DBM})_2\text{Q}_2]^*\text{Q}$, $M = \text{Co, Zn, Cd}$; (3) $[M(\text{DBM})_2\text{Iq}_2]$, $M = \text{Co, Ni, Zn, Cd}$. Single crystal XRD studies confirmed isostructurality of the compounds in each series. The compounds (1) and (3) are electrically neutral molecular metal complexes, with M octahedrally coordinated by two bidentate DBMs and two *trans*-arranged amine ligands. The products (2) are inclusion compounds, where one extra quinoline molecule is included in the crystal as guest.

TGA of the compounds was performed on a TA instrument (Q5000IR, N_2 flow 25 mL/min, linear heating $5^\circ/\text{min}$). The composition of the samples, shown by the formulas above, was unambiguously determined from the thermograms showing the loss of all Q or Iq followed by a plateau of $M(\text{DBM})_2$ (stable up to 280, 293, 266 and 252°C for Co, Ni, Zn and Cd, respectively). The onset temperature of the first dissociation step was taken as a measure of thermal stability of a compound. Several samples of each complex obtained from different solvents were studied to collect statistics. The same stability sequence was observed in series (1) and (3): $\text{Zn} < \text{Cd} < \text{Co} < \text{Ni}$. The differences in T_{onset} significantly exceeded the experimental errors. For example, in series (3) the T_{onset} values were 107(1), 125(2), 142(3) and $155(1)^\circ\text{C}$ for Zn, Cd, Co and Ni, respectively. The results for series (2) deviated from the trend. The results will be discussed with relation to previously reported data.

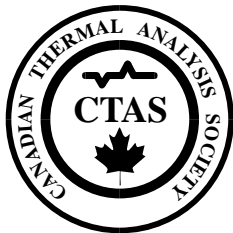


Ammonium nitrate emulsion: physical properties and decomposition using thermal methods

S. Goldthorp, H. Feng, S. Singh, R. Turcotte
Canadian Explosives Research Laboratory
Natural Resources Canada, Ottawa, Ontario, Canada

Ammonium nitrate (NH_4NO_3 or AN) is ubiquitous as the source of nitrogen in commercial fertilizers and commonly used in the manufacture of emulsion explosives. In this latter usage, it is the oxidizing capability of AN which is very desirable. When aqueous solutions of AN are emulsified with a quantity of fuel, the commercial emulsion explosives which are produced may be used in Canada's mining, construction and exploration industries. These products present hazards in manufacture, transport and, of course, end usage. At the Canadian Explosives Research Laboratory (CERL), we seek to better understand these hazards. Little data is available in the open literature linking the physical properties of emulsions to their thermal behaviour. As part of CERL's ongoing hazards research, the physical properties of emulsions manufactured in-house are documented, and the thermal decomposition of these emulsions are quantified.

The physical properties we measure include emulsion droplet size, viscosity, water content, density and thermal conductivity (k). To assess thermal decomposition, we use small scale thermal methods including simultaneous thermogravimetry-calorimetry-infrared spectroscopy-mass spectroscopy (TG-DSC-FTIR-MS) and accelerating rate calorimetry (ARC). For a simple emulsion formulation, we show typical ARC thermal onset temperatures (T_0) ranging from 210 to 230°C, with decomposition gases (H_2O , CO_2 , N_2O , NH_3 , NO_2) detected. As yet, minor variations in the ANE physical properties are shown not to affect T_0 . However, as an emulsion ages, features in the ARC thermograms differ from the fresh sample but T_0 remains unchanged.



Thermal hazard assessment of nitrobenzene /dinitrobenzene mixtures

C. Johnson¹, C. Badeen¹, R. Turcotte¹, E. Hobenshield², and S. Berretta²

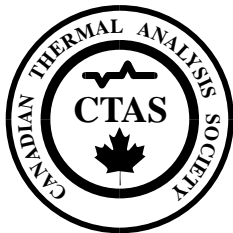
¹Canadian Explosives Research Laboratory, Natural Resources Canada

²NORAM Engineering Constructors Ltd, Vancouver, BC

During the production of nitrobenzene by an adiabatic nitration process, the main byproducts are mono and dinitrophenols as well as picric acid and 1,3-dinitrobenzene. The byproducts formed can become concentrated if a distillation step to remove 'heavy' (i.e., high boiling point) impurities is used. In the present work, representative samples of nitrobenzene containing 20 to 30% dinitrobenzene and less than 1% dinitrophenol, 1% picric acid, and 1% sodium hydroxide were tested by Differential Scanning Calorimetry (DSC) and Accelerating Rate Calorimetry (ARC) in order to investigate their thermal stability relative to that of the pure substances.

The DSC thermal curves for pure nitrobenzene and the various nitrobenzene-dinitrobenzene mixtures exhibited exothermic activity from about 300 to 500°C and enthalpy changes of about $-2.5 \times 10^3 \text{ J g}^{-1}$, which is very energetic. The impurities (dinitrophenol, picric acid, and sodium hydroxide) had no significant effect on the DSC results.

During the ARC experiments, the various nitrobenzene-dinitrobenzene mixtures exhibited exotherms beginning in the 263 - 280°C temperature range. Each of these samples was determined to be less thermally stable than pure nitrobenzene and pure dinitrobenzene. Analysis of ARC data indicates that short-term exposure of nitrobenzene mixtures containing up to 20 wt% dinitrobenzene to temperatures up to 208°C should not pose a serious runaway reaction hazard.



Characterization of thermal properties of FOX-7: A multifaceted thermal analyses

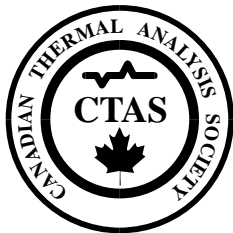
B. Acheson S. Singh and D. E. Jones

Canadian Explosives Research Laboratory, Natural Resources Canada

1,1-diamino-2,2-dinitroethene (FOX-7) is a relatively new explosive that has received considerable attention since its development in the late 1990's. It is a yellow crystalline solid at room temperature and pressure, in which the highly polarised double bond allows many resonance structures to be hypothesized. As an energetic material (EM), the bulk material has low impact and friction sensitivity. This, coupled with its high performance capabilities, make it particularly attractive for potential use in high performance insensitive munitions.

Individual thermal analysis techniques each yield specific relevant information towards the characterisation of EMs. In the case of FOX-7, thermal properties were studied using various calorimetric techniques; differential scanning calorimetry (DSC), high pressure heat flux calorimetry (HFC) and adiabatic calorimetry (ARC). Simultaneous TG-DTA-FTIR-MS was also used.

Three polymorphs exist for FOX-7 in the P-T regime preceding decomposition. One phase is stable, and one is metastable at room temperature. High pressure HFC, designed to operate at pressures up to 38MPa, performed at 0.3 °C/min, was used to investigate the dependence of the phase transition behaviour and decomposition onset temperature on pressure and thermal history. HFC results describe two well defined polymorphic phase changes preceding the decomposition exotherm. In addition, observed peak decomposition temperatures increased with pressure by approximately 7°C over the range tested. Using faster heating rates (2 to 20 °C/min) and smaller sample sizes, DSC curves also exhibit two minor endothermic peaks (representing the polymorphic phase changes), but have two major exothermic peaks, suggesting the presence of two separate polymorphs by decomposition onset. Gram scale sample sizes are used with ARC decomposition experiments. Simultaneous TG-DTA-FTIR-MS provided results which may be used to obtain valuable information to aid in elucidation of decomposition pathways.



Use of calorimetric techniques for the determination of energetics, thermodynamics and kinetics of hydrogen storage in various materials

P. Le Parlouer¹, C. Mathonat¹, N. Garcia²

¹Setaram Instrumentation, Caluire, France; ²Setaram Inc., Newark, USA

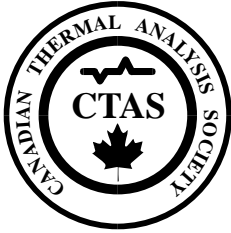
The recent developments in the field of fuel cells and more particularly hydrogen storage under solid form have underlined the usefulness of the calorimetric techniques. Such experimentations enable to perform such studies at variable temperature and pressure, in order to determine the energy associated with the adsorption or desorption of hydrogen. The knowledge of this energy allows assessing the increase in temperature in the course of the reaction. This parameter will be very helpful for the industrialization and the safety of the storage process.

Setaram has especially developed a high-pressure vessel (up to 500 bars) with the SENSYS evo DSC for such investigations. The calorimetric technique will apply for any material used for hydrogen storage under solid form (metal hydride, borohydride, alanate, zeolite, clathrate...).

The main applications of the new high pressure DSC technique in the field of hydrogen storage are:

- the hydrogenation characteristics of various H-storage materials, especially nanomaterials
- the reversibility of the reaction
- the optimization of the temperatures of adsorption and desorption
- the influence of the addition of catalysts
- the safety conditions for the process (especially the absorption phase)
- the kinetic evaluation of the reaction
- the extrapolation and application to industrial hydrogen storage

The C80 calorimeter can also be used to investigate the production of hydrogen during an hydrolysis reaction (for example borohydride with water).



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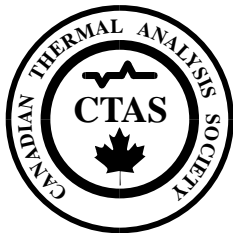
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Controlled Humidity Dynamic Mechanical Analysis

Charles Potter

TA Instruments, New Castle, Delaware, USA

Physical properties of materials are affected by adsorbed moisture as illustrated by the glass transition temperature of Nylon decreasing from + 90 °C to –10 °C with the adsorption of only 6% moisture. Modest changes in the amount of moisture content can result in a dramatic change in the dynamic mechanical and other properties of materials. Dynamic mechanical analysis (DMA) with controlled humidity, in addition to temperature and frequency, provides a powerful technique to examine the properties of materials both at the mechanical and molecular level. Many industries, including plastics, foods, pharmaceuticals and electronics, all benefit from humidity controlled DMA to evaluate the suitability of a material for its intended use and to understand the material fundamentals.



Effect of zinc(II) doping on thermal and optical properties of potassium hydrogen phthalate (KHP) crystals

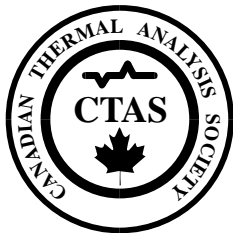
S. Parthiban¹ S. Murali¹ G. Madhurembal² S. P. Meenakshisundaram¹ and
S. C. Mojumdar³

¹Department of Chemistry, Annamalai University, Annamalainagar, India

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³Department of Chemical Engineering and Applied Chemistry, University of Toronto

The influence of doping the transition metal, Zn(II) on potassium hydrogen phthalate (KHP) crystals has been studied. A close observation of FT-IR and XRD profiles of doped and undoped samples reveals some minor structural variations. It appears that the crystal undergoes considerable lattice stress as a result of doping the bivalent zinc. Furthermore, the possibility of cation vacancies aroused owing to the substitution of K^+ by Zn^{2+} could result in a defective crystal system. Energy dispersive spectrum reveals the incorporation of Zn(II) in the crystalline matrix of KHP crystals. Differential scanning calorimetry (DSC) and TG-DTA studies reveal the purity of the sample and no decomposition is observed up to the melting point. Small quantity additions of Zn(II) enhance the fluorescence intensity of KHP crystals. The doping results in morphological changes and significantly improves the second harmonic generation efficiency of the host crystal.



Os(VIII)- Doping effects on the properties and crystalline perfection of potassium hydrogen phthalate (KHP) crystals

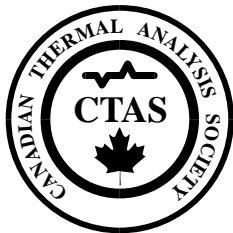
K. Muthu¹, G. Bhagavannarayana² C. Chandrasekaran, S. Parthiban¹, S. P. Meenakshisundaram¹ and S. C. Mojumdar³

¹Department of Chemistry, Annamalai University, Annamalainagar, India.

²Materials Characterization Division, National Physical Laboratory, New Delhi, India.

³Department of Chemical Engineering and Applied Chemistry, University of Toronto

The effect of dopant, Os(VIII)- on the growth process, crystalline perfection and properties of potassium hydrogen phthalate (KHP) single crystals grown by a slow evaporation solution growth technique has been investigated. XRD analysis of black colored doped specimen reveals slight structural changes as a result of doping. The scanning electron micrographs exhibit defect centers and crystal voids. The complex formation of KHP with Os(VIII) is evidenced by the PL spectra since λ_{\max} of the doped specimen is shifted considerably and the fluorescence intensity enhanced sharply. The high resolution X-ray diffraction (HRXRD) studies used to evaluate the crystalline perfection reveal some features on the ability of accommodating the dopant in the crystalline matrix. The diffraction curve (DC) patterns indicate that the transition metal predominantly occupies the interstitial positions. The heavy and high valent transition metal doping depresses the second harmonic generation (SHG) efficiency owing to the deterioration of crystalline perfection disturbing the charge transfer and nonlinearity.

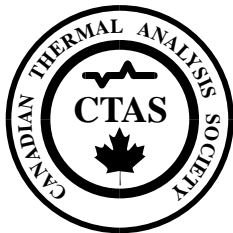


Effect of storage time on the oxidation enthalpy of pyrite

S. C. Mojumdar, I. Bylina, V. G. Papangelakis

Department of Chemical Engineering and Applied Chemistry, University of Toronto

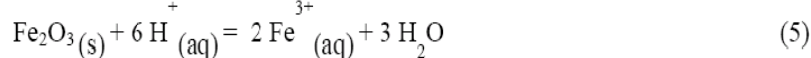
Pyrite (FeS_2) and other sulfide minerals' oxidation data during storage in contact with air are very important for mining and metallurgical processes. Pyrite is associated with other sulphide minerals, which are major carriers of base metals such as nickel, copper and zinc. In the metals industry is often subject to oxidative dissolution under oxygen pressure in aqueous solutions at elevated temperatures in pressure vessels, by a process that is known in the field of hydrometallurgy as Pressure Oxidation. In the industrial practice, the oxidation of pyrite and its polymorph marcasite during storage under normal atmospheric conditions prior to Pressure Oxidation is also a known but not well-studied process. The purpose of this study was to evaluate the heats of oxidation of freshly ground vs. stored (for a year in contact with air) pyrite by calorimetric measurements. The amount of the heat evolved under Pressure Oxidation conditions is important for the heat balance and optimization of the autoclave design in the hydrometallurgical industry. The present study was performed with a Setaram DSC80 equipped with a commercial mixing cell on pure pyrite mineral particles (Valdenegrillos, Spain) at 150 °C and partial oxygen pressure of 3.4 MPa. A calorimetric method for determining the enthalpy of Pressure Oxidation of sulfide minerals has been used to evaluate the enthalpies of oxidation of freshly ground as well as stored pyrite. Measurements showed that pyrite stored over time results in greater heat evolution during oxidative leaching. A mechanism for this phenomenon is proposed.

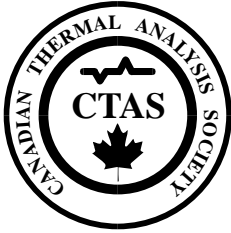


Influence of Mg on hematite solubility in sulphuric acid solutions at elevated temperature

S. C. Mojumdar, M. Reird and V. G. Papangelakis
Department of Chemical Engineering and Applied Chemistry
University of Toronto

Chemical modeling of aqueous electrolyte solutions is becoming increasingly important in the development, analysis, design, and control of hydrometallurgical processes. It is a very powerful tool to predict and understand the behavior of complex aqueous processing systems. Equally powerful is the educational aspect associated with building such models. In recent years, chemical modeling has undergone tremendous development. The new capabilities of various softwares have changed the way engineers simulate aqueous solutions in hydrometallurgical processes. This paper presents new developments and strategies to model the chemistry of high temperature aqueous processing systems. Iron is a surrogate oxygen transfer agent in high-temperature oxidative pressure leach processes for the recovery of base and precious metals. However, iron as hematite (Fe_2O_3) has limited solubility in high temperature aqueous solutions even in the presence of acid. The amount of dissolved iron that is sustained in solution dictates the leaching kinetics. In the absence of on-line sensors that can measure dissolved iron and pH at elevated temperatures, only solution chemistry models offer the ability to access these values based on bulk stoichiometric measurements. To build and calibrate such models, so that they are relevant and accurate under the complex and multi-component industrial environments, accurate experimental data under "clean" conditions are very useful. In this work, such clean experiments in a corrosion-resistant titanium vessel revealed that hematite solubility increases with acid concentration at high-temperatures, but decreases with the addition of MgSO_4 . Our modelling results in the same conditions have also confirmed these findings and a good agreement between modelling and experimental result has been found. The model speciation results indicate that almost all the MgSO_4 dissociates into $\text{Mg}^{2+}(\text{aq})$ and $\text{SO}_4^{2-}(\text{aq})$. The released sulphates reacts with $\text{H}^+(\text{aq})$ in solution to form bisulphate ion, the dominant H_2SO_4 species at higher temperature. The resulting drop in $\text{H}^+(\text{aq})$ concentration reduces the amount of soluble iron (see Equations 1-3).





Thermal and porosimetric analysis used for microstructure characterization of metakaolin sand blended Portland cement mortar

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Metakaolin represents in civil engineering silica-aluminate-based pozzolan which is suitable as composition of blended cements. The content of $\text{Ca}(\text{OH})_2$ is decreased and the amount of CSH gel and additional gel-like alumina-containing phases is increased as a result of reaction of metakaolin with free CaO during cement hydration. Consequently, when metakaolin is blended with Portland cement – the strengths of related cement composites are increased and pore structure is improved. This is connected with reduced permeability.

Two types of raw material – original kaolin sand (OKS I and OKS II) were used for experiment. Original kaolin sands were transformed (1 hour at 650°C with 10 °C/min temperature increase) to burnt kaolin sands (BKS I and BKS II) with pozzolan properties. Contents of decisive mineral (metakaolinite) in burnt kaolin sands are as follows:

BKS I (fraction 60 μm): 20 %; BKS II (fraction 60 μm): 36 % and BKS II (fraction 100 μm): 31 % by mass.

Mortars with blends of Portland cement with metakaolin and standard sands were prepared: MK type I (60 μm) – 5 and 10 % cement substitution; MK type II (60 μm) – 5 and 10% substitution and MK type II (100 μm) – 5, 10, 15 and 20% substitution. Reference mortar with 100 % of Portland cement was prepared for comparison. All prepared mortars were adjusted on the constant workability 180 ± 5 mm flow. Significant increase in compressive strengths was found (after 90-day water cure). Refinement of pore structure in mortars with metakaolin sands (opposite to reference mortar) was revealed. These facts have confirmed the high efficiency of pozzolan reaction in tested systems.