

Chapter 7

Overall conclusion

Characterisation of materials (the core of the current study) is a continually growing and an important component of science in general. It is mainly used to determine the properties (chemical and physical), causes of certain behaviours (e.g. reactivity), design of materials with specific properties, composition (identity and amounts of chemical constituents) of materials, etc. Many different techniques and test methods have been developed to investigate specific aspects of materials. Therefore, the capabilities, relevance, strengths and weaknesses in various techniques have to be considered carefully before deciding on the techniques for analysis. This chapter presents the systematic way followed in selecting the primary technique applied to samples in the current study by outlining four major types of instrumental analysis, namely, elemental analysis, phase analysis, surface characterization and non-destructive testing. For each type of instrumental analysis some related, common and useful techniques are discussed in terms of their advantages and disadvantages (i.e. applicability to the samples studied). The last section outlines the major conclusions drawn from the investigation of the samples in the current study and the future work.

7.1 Elemental analysis

The first step in the characterisation of materials is elemental analysis. There are techniques that give information on elemental composition of samples such as X-ray fluorescence spectroscopy (XRF), particle induced X-ray emission (PIXE), inductively coupled plasma (ICP), neutron activation analysis (NAA), atomic absorption (AA), X-ray photoelectron spectroscopy (XPS), etc. The techniques discussed in this section are X-ray fluorescence spectroscopy (XRF), particle induced X-ray emission (PIXE), inductively coupled plasma (ICP) and neutron activation analysis (NAA).

7.1.1. X-ray fluorescence spectroscopy (XRF)

X-ray fluorescence is the process of emission of X-rays. A sample is normally irradiated with X-rays, which are either absorbed by atoms or scattered in the material. During absorption the energy is absorbed to the innermost electron. However, if the energy is high enough electrons are knocked off from the inner energy levels/shells. The relaxation of the atoms to their stable conditions is accompanied by the return of electrons from the outer shells to the inner shells giving off characteristic X-rays in the process. Since each element has a unique set of shells, each element produces X-rays at a unique set of energy. XRF measures the elemental composition of a sample [1]. The XRF analysis method is in itself non-destructive, but sample preparation is required. Large sample sizes (> 2 g) are required. The advantages of XRF include rapid analysis, spectral coverage of most elements, good precision and accuracy [2]. Energy dispersive XRF has been used mainly for assessment of surface heavy metal contamination [3, 4].

7.1.2. Particle induced X-ray emission (PIXE)

In PIXE, the sample is irradiated with a beam of α -particles (or protons). One electron of an atom-core orbital is ejected on impact. As the electrons reorganises themselves to fill the vacancies created by the ejection, X-rays of characteristic energy are emitted [5]. For instance, if an electron is ejected from the K shell, the K-emission spectrum can contain several bands (due to the dropping of electrons from other different higher energy levels to fill the K shell vacancies), which are denoted with Greek letters. The energy of these X-rays, which is proportional to the amount of energy separating the two orbitals, is characteristic of the emitting element [1]. PIXE's sensitivity is highest for Fe and neighbouring elements with similar Z number (~ 20). For heavy elements, e.g. selenium (Se) or cadmium (Cd), PIXE analysis is not so convenient. The analysis of elements with atomic number lower than 15 can be done best with particle induced gamma-ray emission (PIGE) method [6].

7.1.3. Laser induced breakdown spectroscopy (LIBS)

LIBS measurements consists of spectral and time resolved analysis of the atomic and ionic emission lines generated at the surface of a sample after focusing with an intense nanosecond laser pulse [7]. It gives the emission lines, which are spectral signatures of each element [8]. The relative intensities can be used for the quantitative determination. No sample pretreatment is required. LIBS gives rapid qualitative and possibly *in situ* analysis [9]. LIBS has, however, not yet overcome the experimentation stage to become a routine methodology because of different experimental configurations reported in the literature. Under optimal experimental conditions LIBS is minimally destructive resulting in the formation of a small crater with typical diameters around 40 μm and depth of no more than 10 μm [9, 10]. The spatial resolution of LIBS is superior to that of XRF [10]. The fact that a single laser pulse measurement is complete in less than a second, offers an unparalleled speed to the technique.

Various researchers have applied LIBS to the investigation of artworks and archaeological objects. LIBS has been used to study, qualitatively and quantitatively, the decorative films applied to artworks, such as glazed pottery [11], painted plaster [12], archaeological ceramics and metal artifacts [13], pigments artworks such as in easel and oil paintings [10, 14, 15] and in ancient manuscripts [10]. The application of LIBS provides rapid, *in situ*, depth profile and practically non-destructive determination of pigments in painted artworks [15]. The results obtained using LIBS have been used, among other things, to elucidate manufacturing processes of artwork, its actual degree of conservation and presence of residual surface decorations [11].

7.1.4. Inductively coupled plasma (ICP)

Atmospheric pressure inductively coupled plasmas are flame-like electrical discharges used for speciation, elemental and isotopic ratio analysis [16]. Argon ICPs are remarkable vaporisation-atomisation-excitation-ionisation sources for atomic emission and mass spectrometry. In ICP, plasma is used to excite elemental electrons, which produce photons

(in the form of energy spectrum) unique to that element. ICP is a multi-element method that is suitable for the determination of many elements under the same or different working conditions. There are two common types, which are inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectroscopy (ICP-MS). They are both used for bulk elemental analysis of any material or substance, with the exception of H, O, N, F, Cl and Br. It detects elemental concentrations in the range of parts/million or trillion with the aid of a calibration curve [17, 18]. ICP-OES requires dissolution procedures, are time consuming and can induce loss of some volatile elements (e.g. As, Pb, Se, Sb and Zn) [19].

7.1.5. Neutron activation analysis (NAA)

NAA was traditionally applied to cosmochemical and geochemical problems [20]. The detectors may either be high-resolution Ge(Li) γ -rays (high energy photon) detectors for trace elements [21, 22] or low energy photon detectors (LEPD) [23]. NAA is a multi-element method for analysis of a wide variety of silicate rocks [21]. The detection limit is 0.1 – 100 ppm [21], with moderate accuracy and precision for a number of trace elements [22]. Sample preparation (grinding, mixing with polyethylene wax or graphite and pelletisation) is required [23]. The use of NAA is relatively costly and time consuming [19].

Elemental characterisation is a method of choice for materials obtained from metallurgical processes, because these processes often involve the formation of metallic objects from a single or few specific elements. For instance, techniques such as ICP-MS and ICP-OES have been used to characterise bullet lead alloys [24, 25]. The results of which helped to determine the purity and origins of the samples concerned [26]. Other techniques such as PIXE are often applied to objects made from various precious metals to determine the composition, homogeneity in depth and at the surface [27]. Such studies often reveal, for instance, the original goldsmith techniques, which include the gilding process of ornaments and artifacts.

In the case of more complex materials, such as cement and clay based objects (see sections 1.2 and 2.1), their physical properties, e.g. wettability, particle size, etc., influence material properties. Wettability can be defined as a process in which a liquid covers part or the whole surface of a solid phase. Wettability of cement depends on the free surface energy of adsorption of a methyl group, ΔG_{CH_2} (commonly denoted as γ_s^d , dispersive component of the surface energy at solid-vapour interface), and water to cement (W/C) ratio [28 - 30]. The higher the W/C ratio, the more pronounced is the initial decrease of γ_s^d . The higher the W/C, the higher the interacting sites at the surface [29]. The technique used to measure γ_s^d is contact angle measurement [29, 30]. The contact angle is greater than zero when the liquid covers only a part of the solid phase and equals zero when the whole surface of a solid phase is covered [31]. The contact angle measurement technique measures the angle formed between the liquid drop interface and the solid surface at the point of three-phase contact (the contact point) [32].

The particle size of the constituent components of the cement influences the properties such as strength and setting times, etc [33]. One of the common techniques used to measure the particle size is photon correlation spectroscopy also referred to as dynamic light scattering (DLS). It involves the measurement of Brownian motion and relates this to the particle size, through a mathematical equation [34]. The important basis for the Brownian motion is that small particles move quicker and larger ones move more slowly.

In other cases, such as the design of materials with specific properties, additional information is needed to characterise such materials. The knowledge of elemental composition is not sufficient in the evaluation of characteristics such as colour, hardness, durability and reactivity. For instance, the colour of the pigment is determined by specific compounds, particle size, dispersing media, etc. [35a]. The durability of the material may be defined as the resistance to the environment in which the material will be exposed [35b]. This property can only be evaluated from the results of specific tests carried out, e.g. weathering tests, lightfastness tests, curing in water and heat treatment, in terms of

pigments and cement or concrete [35b, 36]. Hardness is another property of the material mainly evaluated by specific standard tests, such as Barcol Hardness [37].

The reactivity of a material can also be described in terms of chemical stability. Materials such as pigments are usually tested for chemical stability during which the pigment is exposed (for a set time) to chemical environment in which it will be used and the effects are then evaluated [35b]. The reactivity of other materials such as cement and fly ash is evaluated by exposing the material to the environment of application, e.g. water vapour and carbon dioxide in air, and then determining the heat of hydration (related to the amount of water taken up) and the content of calcium hydroxide (related to the measure of carbon dioxide that reacted with lime, CaO, an important component in the such samples) [38].

The elemental information plays a very limited part in the characterisation of materials. It is sufficient in the determination of purity of objects made from pure metals or even alloys. However, its application to the evaluation of physical, some chemical and unique properties does not yield useful results, even though, in some cases, the elements present may indirectly influence the desired properties.

7.2. Chemical phase analysis

At an advanced level of material characterisation it is important to determine in what form (chemical phases) various elements occur in a sample of interest. The techniques available for phase analysis are X-ray diffraction (XRD), Raman spectroscopy, extended X-ray absorption fine structure (EXAFS), etc. The techniques discussed in this section are XRD and Raman spectroscopy.

7.2.1 X-ray diffraction (XRD)

XRD is a qualitative and quantitative analytical technique for analysis of various crystalline compounds present in solid and powder materials [39]. This technique uses the phenomenon of X-ray diffraction by the sample crystal to reveal the details of the structure at

the atomic level. The identity of the sample is determined by comparing its diffraction pattern to that of a known compound in the database. The shapes of the peaks give an indication of the degree of crystallinity [40]. Highly crystalline materials give narrow peaks, while poorly crystalline materials and very small crystals give broad XRD peaks and are thus difficult to identify. The sample size has to be above 2 g and be in powder or crystal form. The XRD spectrum of the crystalline silicon oxide (quartz, α -SiO₂) normally shows a very narrow intense characteristic peak around 2θ value of 27° (Si(111) peak) [41]. Due to high crystallinity and corresponding isolated narrow and intense XRD peak of quartz, this substance is often used as an internal standard for XRD quantitative analysis. The relative content is determined from the peak intensities.

7.2.2. Raman spectroscopy

The basic principles and theory of Raman spectroscopy are given in chapter 3. This technique was instrumental in characterisation of iron oxide polymorphs, some of which have the same chemical formulas but different structures, because of its sensitivity to chemical phases based on structural variations. Details are provided in section 2.3 and chapter 6. Liem et al. [42] also showed that Raman spectroscopy can distinguish between various phases of silicon oxide with same chemical formulas but different structure [42].

7.3. Surface characterisation

The next step to follow (after phase determination) in the characterisation of materials is to measure the texture of the sample to determine properties such as the particle size, faults, domain structure, etc. Applicable techniques include light microscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), etc. The particle size is important in some materials because it often influences the properties of the materials [43]. For instance, particles in the nano scale size range can cross the fenestration in the epithelial lining (in e.g. liver) and are generally taken up efficiently by the cells [44]. Therefore, nanoparticles can be used for drug delivery systems [45].

Faults in materials may include damage such as cracks, pores, etc. The presence of cracks on materials may be the source of material failure or influence the performance thereof. The introduction of faults in construction materials (e.g. concrete, matrix composites) may be beneficial and sufficient to fully relax the energy (tension) [46].

Domain structures results when a material undergoes phase separation, in a length of few tens of nanometers, due to the intrinsic incompatibility between two different segments (e.g. hard and soft) [47]. The presence of domain structures is a primary source of hysteresis and cycling softening [48].

7.3.1. Light microscopy

Light microscopy normally uses a polarising optical microscope with reflected and transmitted light together with a mercury lamp and filters. Therefore, the objects as small as a few micrometers can be observed while sample degradation is rare. However, sample preparation is required [49, 50].

7.3.2. Scanning electron microscopy (SEM)

SEM is an optical technique that uses high-energy electrons to bombard the surface of a specimen. When the electrons collide with the atoms of the specimen they dislodge electrons from these atoms as radiated secondary electron. The secondary electrons are collected at the detector, usually a phosphorescent screen, where a secondary electron image of the atoms of the specimen is formed [51]. The main results of SEM are particle size (and in some instruments size distribution) and morphology (texture and shape) [52]. The sample has to be in solid form and only a few milligrams are required. Sample preparation involves coating with a thin layer of carbon or gold to create a conducting surface for samples, because most surfaces often accumulate electrons/charge during the electron bombardment. The recovery of the sample in its original form is not possible after analysis. Both amorphous and crystalline samples can be analysed using SEM.

7.3.3. Atomic force microscopy (AFM)

AFM is also an optical technique. It measures surface properties through an interaction between the probe (a commercial micro-fabricated tip) and the surfaces, while moving across the sample recording the x, y and z coordinates [53]. The probe is a tip on the end of cantilever, which bends in response to the force between the tip and the sample. The instrument can operate in a contact mode (where the probe is in contact with sample analysed) or in a non-contact mode (where the probe does not touch the sample surface) [53]. AFM does not require sample preparation and can be operated in air or liquids [54]. It also gives information on particle size, morphology and 3-dimensional images [53, 55]. It has higher spatial resolution than that of SEM [56, 57].

7.4. Non-destructive testing

This is the type of analysis during which the physical and chemical integrity of the sample cannot be altered. Therefore, no sample preparation or modification whatsoever, is allowed. Examples of samples that require non-destructive testing are valuable objects, manufactured articles (e.g. silicon chips), objects of art, archaeological and other unique samples.

The main reasons for non-destructive testing may be the need for preservation, reconstruction, authentication, study of properties and technologies as well as *in situ* analysis (e.g. of blood, skin and brain in medical applications). The samples currently under study are clay-based archaeological objects and related iron oxide pigments. Therefore, information on chemical phases needs to be obtained non-destructively.

The elemental results will be useful to some limited extent and more information will still be required if the forms of the constituent components are to be ascertained. The only elemental techniques that are non-destructive are laser-based, such as PIXE. However, not

all elements can be detected by PIXE. LIBS is another technique which, in most applications may be viewed as non-destructive, but it is technically not non-destructive.

The surface characterisation properties that were important in the current study relate to the particle size and shape. These properties influence mainly the colour of the objects and pigments themselves. However, all surface techniques mentioned above require sample preparation and therefore were not suitable for non-destructive analysis of archaeological samples. SEM was applied only to the synthesised iron oxides for particle size and shape determination.

Techniques that give information on phases non-destructively are essential in the current study, as explained above. XRD is one of the most robust techniques in the determination of chemical phases but it is destructive and cannot detect amorphous phases and small crystallites. Therefore, Raman spectroscopy may be the alternative because it detects amorphous and crystalline phases non-destructively, has *in situ* capabilities, show high sensitivity and specificity (see section 1.2.3). Therefore, Raman spectroscopy with the use of known or literature assignments has been selected and successfully applied to the characterisation of components in earthenware archaeological objects and pigments obtained from iron waste materials.

7.5. Application of Raman spectroscopy

7.5.1. Earthenware archaeological objects

The determination of chemical components in earthenware archaeological objects of Chinese and South African origin confirmed the effectiveness of Raman spectroscopy in the analysis of these objects. Some chemical components identified were crystalline aluminosilicates, non-crystalline aluminosilicates, inorganic minerals and pigments. Crystalline clay minerals identified in South African objects were kaolins, illite and montmorillonite, and appeared to have been mixed, either intentionally or unintentionally. The Chinese clay objects contained mainly kaolins. The non-crystalline aluminisilicates

identified in samples from the two origins were mullite, anhydrite, feldspar and calcium silicates (CaSiO_3). Other inorganic compounds, namely, quartz, rutile, gypsum, phosphates and calcium carbonate, were also detected by Raman spectroscopy. Some pigments such as hematite (red-brown in colour) and amorphous carbon (gray and black in colour) were also identified in both Chinese and South African objects.

The processing conditions were deduced from the above chemical components identified in respective samples. The processing temperatures of Lydenburg, Graskop and Rooiwal were below $800\text{ }^\circ\text{C}$ and those for Makahane reached some temperatures between $800\text{ }^\circ\text{C}$ and $1100\text{ }^\circ\text{C}$. The corresponding processing temperatures for the Chinese samples were above $800\text{ }^\circ\text{C}$. The chemical components identified further suggested that the objects were most likely fired in an open fire. All the samples appear to have been processed under oxidative atmosphere.

Clay objects from different origins have been distinguished. It has been shown that Raman spectroscopic results can be used to deduce the raw materials and processing conditions used in the production of earthenware objects. The pigments that lend colour to the objects have also been identified. The use of Raman spectroscopy further showed that earthenware objects from different origins have different chemical components. The chemical components obtained also revealed differences and similarities between processing conditions used by corresponding potters in making the objects. It has also been found that different potters in the same vicinity tended to use similar raw materials (either obtained from the same source or mixed in a similar fashion) and processing conditions, as indicated by the overlapping chemical components from different origins. The results further revealed that the most likely firing mode was an open fire.

7.5.2. Iron oxide pigments

The present study proved that chemical substances (containing mainly sulphates of Fe^{2+} and Fe^{3+}) derived from mill scale iron waste can be used as the raw materials for the

preparation of good quality magnetite and goethite. Magnetite and goethite were in turn thermally converted to maghemite and hematite, respectively.

The characterisation of the products was successfully carried out using Raman spectroscopy, the results of which were confirmed by XRD, FT-IR and in some cases XRF spectroscopy. Raman spectroscopy revealed reduced crystallinity made apparent by shifting or broadening of characteristic bands. This was also observed in the XRD results. The results obtained further revealed that the methods applied in preparing various iron oxides were generally specific and gave only the intended product, except in the case of goethite synthesis. The goethite product was contaminated with some traces of the hematite polymorph detectable only by Raman spectroscopy. In general the products were of high purity, as indicated by very low levels of contamination in cases where it was detected.

In the end the complete chemical characterisation of earthenware archaeological objects should entail the qualitative analysis of aluminosilicates (crystalline or non-crystalline), other inorganic compounds and pigments, all of which are the main components (either added as raw materials or evolved during processing). The techniques applied for this purpose should show capabilities of rapid measurement, high sensitivity, specificity, non-destructive analysis, free of sample preparation, *in situ* analysis, detection of crystalline and amorphous phases and give unambiguous results.

The present study has met the above requirements. The study has succeeded in identifying a number of aluminosilicates (various clay minerals, feldspars and silicates), other inorganic compounds (e.g. titanium dioxide, calcium carbonate and phosphates) and pigments (various iron oxides and amorphous carbon) the results of which laid a fair basis for chemical characterisation of the samples involved. The investigation of both the Chinese and South African samples and the results thereof confirmed the relevance and appropriateness of Raman spectroscopic application to the earthenware archaeological objects in general.

The analysis of iron oxides from iron waste (i.e. mill scale, which normally contains other substances besides iron and its related compounds) in a way presented a practical scenario of the analysis of multi-components of crystalline and non-crystalline compounds in a single sample as is common with earthenware archaeological objects. The results obtained further confirmed the sensitivity, *in situ* capability and specificity of Raman spectroscopy. The mill scale iron oxide results further added credit to the quality of the results obtained for earthenware archaeological objects (particularly for iron oxides identified therein).

Therefore, it can be concluded that the Raman spectroscopy has been found to be the relevant and appropriate technique for the full characterisation of earthenware archaeological objects (and their related iron oxide pigments) of Chinese and South African origin.

7.5.3. Future work

For earthenware archaeological objects the future work will involve the quantitative analysis of chemical components as identified by Raman spectroscopy. The most appropriate tool for such multi-component samples is chemometrics (i.e. multivariate analysis). The determination of the amount of each chemical component will form a sound basis for the reconstruction of these clay objects. The raw materials for the clay objects may be obtained from the quarries (if known) in the vicinity of each collection or prepared from pure components as identified by Raman spectroscopy. The pottery thus formed will provide further evidence and a more accurate level of appropriateness of Raman spectroscopic application to these types of samples. The combination of infrared and Raman spectroscopy in the non-destructive investigation of clay objects in this study could reveal even more valuable information. This can only be achieved by analysing same areas/spots on the sample. The newly emerging focusing accessories that can be simultaneously linked to both infrared and Raman spectroscopy could be very useful.

For iron oxide pigments the future work will involve the determination of the actual pigment properties of magnetite, goethite, hematite and maghemite prepared from mill scale. These

properties include tinting strength, hiding power, oil absorption, colour strength, choice of stabiliser and its compatibility with the pigment. Furthermore the causes of discolourisation of iron oxides (magnetite being the worst affected) with time could be investigated. Such a study will also clarify the mechanism of pigments discolourisation at the same time providing insight into how the process can be slowed down or stopped completely. This investigation would limit the use of stabilisers and subsequently the costs of iron oxide pigments will decrease.

7.6. References

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1. R. Jenkins, *Anal. Chem. Part A* **56**, 1099 (1984).
 2. X. Hou and B. T. Jones, *Microchem. J.* **66**, 155 (2000).
 3. G. A. Rano, R. E. Enwall, W. H. Cole, C. A. Kuharic and G. S. Duggan, *Environ. Sci. Res.* **42**, 155 (1991).
 4. P. J. Potts, P. C. Webb, O. Williamsons-Thorpe and R. Kilworth, *Analyst* **12**, 1253 (1995).
 5. M. Bertrand, G. Weber and B. Schoeffs, *Trends Anal. Chem.* **22**, 254 (2003).
 6. A. K. Kiss et al *J. Radioanal. Nucl. Chem.* **89**, 123 (1985).
 7. V. Lazic, R. Barbini, F. Colao, R. Fantoni, A. Palucci, *Spectrochim. Acta Part B* **56**, 807 (2001).
 8. D. A. Rusak, B. C. Castle, B. W. Smith and J. D. Wineforder, *Crit. Rev. Anal. Chem.* **27**, 257 (1992).
 9. E. Tognoni, V. Palleschi, M. Corsi and G. Cristoforetti, *Spectrochim. Acta Part B* **57**, 1115 (2002).
 10. D. Anglos *Appl. Spectrosc.* **55**, 186A (2001).
 11. F. Colao, R. Fanti, V. Lazic and V. Spizzichino, *Spectrochim. Acta Part B* **57**, 1219 (2002).
 12. A. Prysbaert, K. Melessanaki and D. Anglos, *J. Archaeol. Sci.* **33**, 1095 (2006).
 13. K. Melessanaki, M. Mteo, S. C. Ferrence, P. P. Betancourt and D. Anglos, *Appl. Surf. Sci.* **197**, 198 (2002).

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14. L. Burgio, R. J. H. Clark, T. Stratoudaki, M. Doulgeldis and D. Anglos, *Appl. Spectrosc.* **54**, 463 (2000).
 15. D. Aglos, S. Curtis and C. Fotakis, *Appl. Spectrosc.* **51**, 1025 (1997).
 16. H. Watenabe, M. Aihara and M. Kiboku, *Bunseki Kagaku* **39**, 61 (1990).
 17. M. J. Tominson, L. Lin and J. A. Caruso, *Analyst* **120**, 583 (1995).
 18. C. B'Hymer and J. A. Caruso. *J. Chromatogr. Part A* **1114**, 1(2004).
 19. O. Dogan and M. Kobya, *J. Quant. Spectrosc. Radiat. Transfer* **101**, 146 (2006).
 20. J. Hertogen in P. J. Elving, V. Krivan and I. M. Kolthoff (eds), *Treatise on analytical chemistry*, Vol. 14, 2nd edns., Wiley, New York p. 713 (1986).
 21. G. E. Gordon. K. Randle, G. G. Goles, J. B. Corliss, M. H. Buson and S. S. Oxley, *Geochim. Cosmochim. Acta* **32**, 369 (1968).
 22. J. Hertogen and R. Gijbels, *Anal. Chim. Acta* **56**, 61 (1971).
 23. R. Gijbels , *Inorg. Chim. Acta* **140**, 295 (1987).
 24. R. O. Keto, *J. Forensic Sci.* **44**, 1020 (1999).
 25. E. Randich, W. Dverfeldt, W. McLendon and W. Tobin, *Forensic Sci. Int.* **127**, 174 (2002).
 26. J. L. Ruvalcaba-Sil and G. Demortier, *Instr. Methods Phys. Res. Section B* **113**, 275 (1996).
 27. J. L. Ruvalcaba-Sil and G. Demortier, *Instr. Methods Phys. Res. Section B* **130**, 297 (1997).
 28. A. W. Momber, *J. Adhesion* **78**, **203** (2002).
 29. K. Benzarti, C. Perruchot and M. M. Chehimi, *Colloid Surface Part A* **286**, 78 (2006).
 30. J. Lawrence, *Mater. Sci. Eng. Part A* **356**, 162 (2003).
 31. A. Gijbels, *Int. J. Heat Mass Transfer* **48**, 4829 (2005).
 32. T. D. Blake, *J. Colloid and Interf. Sci.* **299**, 1 (2006).
 33. C. Liu, H. Shau, F. Chen and H. Zheng, *Biomaterials* **27**, 5003 (2006).
 34. K. Kita-Tokarczyk, J. Grumelard, T. Haefele and W. Meier, *Polymer* **46**, 3540 (2005).
 35. J. A. Kroschwitz and M. Howegrant, *Pigments to powders handling*. In: *Encyclopedia of chemical technology*, 4th ed, John Wiley & sons, New York, Vol. 19, a: p. 26, b: p. 8 (1996).
 36. F. P. Togonal and J. P. Castro-Gomes, *Constr. Build. Mater.* **20**, 1079 (2006).

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37. A. C. Berg, L. C. Bank, M. G. Oliva and J. S. Russell, *Constr. and Build. Mater.* **20**, 515 (2006).
 38. M. R. Jones, A. McCarthy and A. P. P. G. Booth, *Fuel* **185**, 2250 (2006).
 39. K. Norrish and R. M. Taylor, *Clay Miner.* **5**, 98 (1962).
 40. C. P. Nicolaidis, N. P. Sincadu and M. S. Scurrill, *Catal. Today* **71**, 429 (2002).
 41. V. Kapaklis, C. Politts, P. Pouloupoulos and P. Schweiss, *Mater. Sci. Eng.* **124 – 125**, 475 (2005).
 42. N. Q. Liem, G. Sagon, V. X. Quang, H. Van Tan and P. Colomban, *J. Raman Spectrosc.* **31**, 933 (2000).
 43. W. H. Hunter, Jr. *JOM* 13 – 18 (2004).
 44. K. Bugunia-kubik and M. Sugisaka, *BioSystems* **65**, 123 (2002).
 45. K. Dillen and W. Weyenberg, J. Vandervoort and A. Ludwig, *Pharm. Biopharm* **58**, 539 (2004).
 46. A. Pandolfi, S. Conti and M. Ortiz, *J. Mech. Phys. Solids* **33**, 1505 (2006).
 47. H. J. Qi and M. C. Boyce, *Mech. Mater.* **37**, 817 (2005).
 48. Z. Petrovic and J. Ferguson, *Prog. Polym. Sci.* **16**, 625 (1991).
 49. J. E. Gillot, *Can. J. Earth Sci.* **1**, 121 (1964).
 50. L. Tong and M. Tang, *Cer. Concr. Res.* **21**, 361 (1991).
 51. J. H. Butler, D. C. Joy, G. F. Bradley and S. J. Krause, *Polymer* **36**, 1781 (1995).
 52. H. Shu, W. Yu, Y. Zhao and X. Liu, *J. Food Eng.* **76**, 664 (2006).
 53. R. Pereira, *Biochem. Pharm.* **62**, 975 (2001).
 54. S. Anabousi, M. Laue, C. Lelu, U. Bakowsky and C. Ehrhardt, *Eur. J. Pharm. Biopharm.* **60**, 295 (2005).
 55. M. Oliva, C. Caramella, I. Diez-Perez, P. C. Gorostiza, F. Lastra, I. Oliva and E. L. Marino, *Int. J. Pharm.* **242**, 291 (2002).
 56. L. Mu and S. S. Feng, *J. Control. Release* **76**, 239 (2001).
 57. S.-S. Feng and G. Fluang, *J. Control. Release* **71**, 53 (2001).