References

Alcañiz-Monge, J., Amoros, D.C., Solano A.L. (2001). Characterization of coal tar pitches by thermal analysis, infrared spectroscopy and solvent fractionation. Fuel 80, 41-48.

Andresen, J.M., Luengo, C.A., Moinelo, S.R., Garcia, R., Snape, C.E. (1998). Structural uniformity of toluene- insolubles from heat treated coal tar pitch as determined by solid state ^{13}C NMR spectroscopy. Energy & Fuels 12, 524-530.

Arnesen, A.G., Økstad, S., Innvær, R., Olsen, L. (1979). Operation of Söderberg electrodes. In Proc. of the Elkem seminar on smelting, Rio de Janeiro.Brasil

Arnold, W.P. (1997). Tar. Clinics in Dermatology 15, 739-744.

Asphaug, B and Innvær, R. (1997). Introduction to the Söderberg electrode, Boxer Technologies AS for Elkem Carbon, Kristiansand, Norway.

Austin, T.G. (1945). Shreve's Chemical process industries, McGraw-Hill international editions, Chemical engineering series, 5th edition

Bailey B.L. (1950). Carbon electrode. (United States patent number, 2,527,294 24).

Baron, J.T., A. McKinney, S.A., Wombles, H.R. (2009). Coal tar pitch- past, present and future. Light metals (The minerals, metals and materials society), 935-939

Belekov, E.A. (2001). Formation of graphite structure in carbon crystallites. Inorganic materials 37 (9), 928- 934.

Bergeim, F.H., Leonia, N.J. (1937). Distillation product. (US patent number 2, 066, 386, 5).

Bermejo, J., Granda, M., Mendez, R., Garcia, R., Tascon J.M.D. (1997). Thermal behavior of extrographic fractions of coal tar and petroleum pitches. Fuel 76 (2), 179-187.

Bermejo, J., Menendez, R., Figueiras, A., Granda M. (1995). The role of low molecular-weight components in the pyrolysis of pitches. Fuel 74 (12), 1792-1799.

Bermudez, A., Bullon, J., Pena, F., Salgado P. (2003). A numerical method for transient simulation of metallurgical compound electrodes. Finite elements in analysis and design 39, 83-299.

Bermudez, A., Rodriguez, R., Salgado, P. (2002). A finite element method for the eddy currents problem in an electrode with input intensities as boundary data. Mecanica Computacional XXI, 2557-2568.

Beukes, J.P., Roos, H., Shoko, L., van Zyl, P.G., Neomagus, H.W.J.P., Strydom, C.A., Dawson, N.F. (2013). The use of thermomechanical analysis to characterize Söderberg electrode paste raw materials. Minerals engineering 46-47, 167-176.

Bhatia, G., Aggarwal, R.K., Bahl, O.P. (1987). A relationship for the evaluation of coking values of coal tar pitches from their physical characteristics. Journal of Materials Science 22, 3847-3850.

Blanco, C., Santamaria, R., Bermejo, J., Menendez, R. (2000). A comparative study of air-blown and thermally treated coal-tar pitches. Carbon 38, 517-523.

Brown, M.E. (1988). Introduction to thermal analysis, Techniques and applications. Chapman and Hall, New York, pp. 63-64.

Bruff, W., de Santana, G.S., de Oliveira D.G. (1985). Process for the manufacture of in situ carbon electrodes. (United States patent 4.527, 329).

Bryant, G.W., Lucas, J.A., Gupta, S.K., Wall, T.F. (1998). Use of Thermomechanical analysis to quantify the flux necessary for slag flow in slagging gasifiers fired with coal. Energy & Fuels 12, 257-261.

Bullon, J., Perez A. (2010). Carbon analysis at ferroatlantica I + D, 770-776. (http:www.pyrometallurgy.co.za/infaconXI/074.pdf.Accesed:15 March 2010).

Burgess, W.A., Thies M, C. (2011). Molecular structures for the oligomeric constituents of petroleum pitch. Carbon 49, 636-651.

Casal, E., Vina, J., Bonhomme, J., Granda, M., Menendez, R. (2000). The effects of inherent solid particles on the structure and mechanical properties of coal tar pitch based C-C composites. Journal of Materials Chemistry 10, 2637-264.

Casal, M.D., Canga, C.S., Diez, M.A., Alvarez, R., Barriocanal, C. (2005). Low temperature pyrolysis of coals with different coking pressure characteristics. Journal of Applied Pyrolysis 74, 96-113.

Cebolla, V.L., Vela, J., Membrado, L., Ferrando, A.C. (1996). Coal characterization by thin layer chromatography with flame ionization detection. Chromatographia 42 (5/6), 295.

Cerny, J. (1991). Structural features of coal tar maltenes by FT-IR spectroscopy. Energy & Fuels 5 (6), 781-786.

Chung, D.D.L. (2002). Review Graphite. Journal of materials science 37, 1475-1489.

Codd, L.W., Dijkhoff, K., Fearon J.H, van Oss C.J, Roebersen H.G, Stanford E.G, van Thoor T.J.W. (1971). Materials and Technology Volume II, London: Longman group.

Conroy E.P. (1975). Production of pitch substantially soluble in quinoline. (US patent number 3,928,169, 23).

Dall, D. (2008). 4th year undergraduate chemical engineering project report – Electrode paste quality (Confidential report). North-West University, Potchefstroom, South Africa.

Diaz, C., Blanco, C.G. (2003). NMR: A powerful tool in the characterization of coal tar pitch, Energy and Fuels 17, 907-913.

Coutinho, A.R., Rocha, J.D., Luengo, C.A. (2000). Preparing and characterizing bio electrodes, Fuel processing Technology 67, 93-102.

Cross, C.B., Ecker, R.D., Stein, O.L. (1964). Artificial graphite process. (US patent number 3, 116, 975, 7).

Currie, L.M., MacPherson, H.G., Hamister, V.C. (1955). The production and properties of graphite for reactors. United Nations International Conference on the peaceful uses of atomic energy, Geneva, Switzerland, August 8-20.

de Castro, L.D. (2006). Anisotropy and Mesophase formation towards carbon fibre production from coal tar and petroleum pitches - A Review. Journal of Brazilian Chemical society 17 (6), 1096 -1108.

Dreeskamp, H., Potempa, T., Muller, A. (1989). Aspects of quantitative ^{13}C n.m.r spectroscopy of high boiling oil residues and coal tar pitches. Fuel 68, 972-977.

Enzminger, J.D., Ahlert, R.C. (1987). Environmental fate of polynuclear aromatic hydrocarbons in coal tar. Environmental Technology Letters 8, 269-278.

Feret, F.R. (1998). Determination of the crystallinity of calcined and graphitic cokes by X-ray diffraction. Analyst 123, 595-600.

Fetzer, J.C., Kershaw, J.R. (1995). Identification of large polycyclic aromatic hydrocarbons in a coal tar pitch. Fuel 74 (10), 1533-1536.

Fitt, A.D., Howell, P.D. (1998). The manufacture of continuous smelting electrodes from carbon-paste briquettes. Journal of engineering mathematics 33, 353-376.

Fitt, A.D., Aitchison, J.M. (1993). Determining the effective viscosity of a carbon paste used for continuous electrode smelting Fluid Dynamics Research 11, 37-59.

Fitzer, E., Kompalik, D., Yudate, K. (1987). Rheological characteristics of coal tar pitches. Fuel 66, 1504-1511.

Fuchs, W., Sandhoff, A.G. (1942). Theory of coal pyrolysis. Industrial and Engineering Chemistry 34 (5), 567-571.

Galiguzov, A.A., Kulakov, V.V., Kalugin., D.I., Malakho., A.P., Avdeev, V.V. (2012). Comparative studies of thermal stability of coal tar pitches. Journal of Chemistry and Chemical Engineering 6, 860-865.

Geng, W., Nakajima, T., Takanashe, H., Ohki, A. (2009). Analysis of carboxyl group in coal and coal aromaticity by Fourier Transform infrared (FT-IR). Fuel 88, 139-144.

Gray, M.D., Kimber, G.M., Shipley, D.E. (1976). Manufacture of coke from a coal extract. (US patent number 3, 966, 585, 29).

Griffiths, P.R. and de Haseth, J.A. (2007). Fourier Transform Infrared Spectroscopy.2nd Edition, John Wiley and Sons, Inc Publication USA.

Guillen, M.D., Dominguez, A., Iglesias, M.J., Blanco, C.G. (1995). Fourier Transform infrared study of coal tar pitches. Fuel 11, 1595-1598.

Guillen, M.D., Dominguez, A., Iglesias, M.J., Fuente, E., Blanco, C.G. (1996). Analysis of coal tar pitch: relations between thermal behaviour and composition. Fuel 75 (9), 1101-1107.

Guillen, M.D., Iglesias, M.J., Dominguez, A., Blanco, C.G. (1992). Semi quantitative FT-IR analysis of coal tar pitch and its extracts and residues in several organic solvents. Energy & Fuels 6, 518-525.

Habashi, F. (2004). Clean Technology in the metallurgical Industry. Chemistry for sustainable development 12, 93-98.

Hamister, V.C. (1953). Graphitization of Carbon articles. (United States patent number 2,644,020).

MATLAB, The language of technical computing. http://www.mathworks.com/products/matlab/. (Date accessed: 29 April 2013).

Hussain, R., Qadeer. R. (2000). X-Ray diffraction study of heat-treated graphitized and ungraphitized. Turk J Chem 24, 177- 183.

Ibara, J.V., Cervero, I., Moliner, R. (1989). Structural characterization of low temperature pyrolysis tars and their relation with parent coals. Fuel Processing Technology 2 (2), 135-149.

Innvaer, R., Olsen L. (1980). Calculation of thermal stresses in Söderberg Electrodes, Proceedings: International Union for Electro Heat (UIE), 9th International Congress, Cannes. pp. 2-11.

Innvær, R. (1992). A status for the Söderberg smelting electrode. In *Proc. of UIE, Electrotech 2*. Montreal, Canada.

Innvær, R., Fidje, K., Ugland, R. (1986). Effect of current variations on material properties and thermal stresses in Söderberg electrodes. In *Proc. of INFACON IV*. Rio de Janeiro, Brasil. pp. 321-330.

Innvær, R., Olsen, L., Vatland, A. (1984). Operational parameters for Söderberg electrodes from calculations, measurements and plant experience. In *Proc. of Mintek 50*. Johannesburg, South Africa. pp. 787-794.

Irwin, C. (1998). Carbon products industry. Vision for the future. West Virginia University (WSU) research report pp.4.

Islas, C.A., Suelves, I., Apicella B., Herod, A.A., Kandiyoti, R., Carter, J.F., Li, W. (2003) Structure and composition of coal tars: An attempt to correlate molecular structure with increasing molecular mass. Combustion Science and Technology, 175:775-791.

Janes, M. (1969). Coke production. (United States patent number 3, 451, 921, 24).

Karagoz, Y.B., Rua, M.J., Moore, T., Ledford, L.E., Allen, D.P., Agnello, G., Fleckenstein, T.E. (1994). Graphitization furnace. (US patent number 5,299,225).

King, F.L. (1967). Activated carbon in the preparation of binder pitch. (US patent number 3,355,377 28).

Kortovich, J.W., Micinski, E. (1985). Manufacture of high quality graphite electrodes using calcined anthracite coal as raw material. (US patent number, 4, 534, 951, 13).

Kuznetsov, D.M., Korobov, V.K. (2000). Factors affecting the service life of graphitized electrodes in electric arc furnaces. Metallurgist 44, (5/6), 302-304.

Lewis, I.C. (1982). Chemistry of carbonization, Carbon, 30:6:519-529

Lewis, I.C. (1987). Chemistry of pitch carbonization, Fuel 66, 1527-1531

Lewis, I.C., Howard, R.A. (1995). Graphite electrodes and their production. (United States patent number, 5,413,738 9).

Li, C., Suzuki, K. (2009). Tar property, analysis, reforming mechanism and model for biomass gasification-an overview. Renewable and sustainable energy reviews 13, 594-604.

Li, C., Suzuki, K. (2010). Resources, properties and Utilization of tar, Resources. Conservation and Recycling 54, 905-915.

Liu, Y., Gupta, R., Elliot, L., Wall, T., Fujimori, T. (2007). Thermomechanical analysis of laboratory ash, combustion ash and deposits from coal combustion. Fuel Processing Technology 88, 1099-1107.

Liu, Y., Hodek W., van Heek, K.H. (1998). Characterization of tar, char and gas from pyrolysis of coal asphaltenes. Fuel 77 (9/10), 1099-1105.

Lowry, H.H. (1945). Chemistry of coal utilization, Chapman and Hall Limited, 1280-1370.

Machnikowski, J., Machnikowska, H., Diez M.A., Alvarez, R., Bermejo, J. (1997). Characterization of coal-derived pitches as precursors for advanced carbon materials by chromatographic and related techniques. Journal of Chromatography A 778, 403-413.

Machnikowski, J., Rutkowski, P., Diez, M.A. (2006). Co-treatment of novolac- and resole-type phenolic resins with coal-tar pitch for porous carbons. Journal of Analytical and Applied Pyrolysis 76, 80-87.

Makgato, M.H., Moitsheki, L.J., Shoko, L., Kgobane, B.L., Morgan, D.L., Focke, W.W. (2009). Alkali- assisted coal extraction with polar aprotic solvents. Fuel processing technology 90, 591-598.

Manabile, I.S. (2009). Study of the early stages of carbonization of some pitch material of different composition. MSc dissertation, University of Pretoria.

Manoj, B., Kunjomana, A.G. (2012). Structural characterization of selected Indian coals by X-ray diffraction and spectroscopic techniques. Trends in applied sciences research 7 (6), 434-444.

Marsh, H. (1989). Introduction to carbon science.Butterwoths, London, United Kingdom.

Martin, Y., Garcia, R., Sole, R.A., Moinelo, S.R. (1998). Characterization of pitch by HPLC. Chromatographia 47 (7/8), 373-382.

Mashau, N.S. (2007). The preparation of pitches from Anthracene oils. MSc dissertation, University of Pretoria.

Mason, C.R. (1970). Correlations between pitch binder properties and properties of Söderberg electrodes 49 (2), 165-174.

Matsumoto, T. (1986). Mesophase pitch and its carbon fibers. Pure & Applied Chemistry 57 (11), 1553-1562.

McDougall, I., Smith, C.F.R., Olmstead, B., Gericke, W.A. (2004). Proceedings: Infacon, 10th International Ferroalloys Congress. February 1-4, Cape Town, South Africa. pp. 575-584.

McMurry, J. (1992). Organic chemistry, Third edition. Brooks/Cole Publishing Company, California, pp. 442-479.

Mendez, A., Santamaria, R., Granda, M., Menendez, R. (2008). Structural changes during pitch-based granular composites carbonization. Journal of Material Science 43, 906-921.

Mendez, A., Santamaria, R., Granda, M., Herod, A.A., Kandiyoti, R., Menendez, R. (2003). Influence of granular carbons pitch properties. Fuel 82, 1241-1250.

Mendez, A., Santamaria, R., Menendez, R., Bermejo, J. (2001). Influence of granular carbons on the pyrolysis behavior of coal tar pitches. Journal of Analytical and Applied Pyrolysis 58, 825-840.

Menendez, R. and Granda, M. (2007). Coal-tar pitch utilization. http:digital.csic.es/handle/10261/4943?idioma=en.

Meyer zu Reckendorf, R. (1997). Identification of phenyl-substituted poly aromatic compounds in ring furnace gases using GC-MS and GC-AED. Chromatographia 45, 173-182.

Meyjes, R.P., Venter, J., van Rooyen. U. (2010). Advanced modelling and baking of electrodes. The Twelfth International Ferroalloys Congress, June 6-9, Helsinki, Finland. pp. 779-788.

Miller, D.J., Albers, T., Lewis, I.C. Ball, D.R. (2010). Low CTE highly isotropic graphite. (US patent number 7,658,902 B2).

Miyazaki, T. I., Ikeda, T. (1982). Process for preparing a graphite product. (United States patent number 4,311,682 19).

Montgomery, R.W. (1981). Electric arc furnace electrodes. (United States patent number 4,287,381).

Mora, E., Santamaria, R., Blanco, C., Granda, M., Menendez, R. (2003). Mesophase development in petroleum and coal tar pitches and their blends. Journal of Analytical and Applied pyrolysis 68-69, 409-424.

Nelson, L.R., Prins, F.X. (2004). Insights into the influences of paste additions and levels on Söderberg electrode management Proceedings: Infacon, 10th International Ferroalloys Congress; February 1-4, Cape Town, South Africa. pp. 418-431.

Ord, R.J., Schofield, J.G., Tan. C.G. (1995). Improved performance of Söderberg electrodes. CIM Bulletin 88, 97-101.

Orlov, M.L., (1996). Multi linear regression analysis using Microsoft Excel. Department of Chemistry, Oregon State University.

Painter, P., Starsnic, M., Coleman, M. (1985). Fourier Transform Infrared Spectroscopy. Academic Press Inc, pp. 169-237.

Papole, G., Focke, W.W., Manyala, N. (2012). Characterization of medium-temperature Sasol-Lurgi gasifier coal tar pitch 98, 243-248.

Pappano, P.J., Burchell, T.D., Wilson, D. (2006). High thermal conductivity graphite and method of making. (United States patent number US 2006/0029805 A1).

Perez, M, Grand M, Garcia R, Santamaria R, Romero E., Menendez R. (2002). Pyrolysis behavior of petroleum pitches prepared at different conditions. Journal of Analytical and Applied Pyrolysis 63, 223-239.

Perez, M., Granda, M., Santamaria, R., Morgan, T., Menendez, R.A. (2004). Thermoanalytical study of the co-pyrolysis of coal tar pitch and petroleum pitch. Fuel 83, 1257-1265.

Prauchner, J.M., Pasa V.M.D, Otani, C., Otani S. (2001). Characterization and thermal polymerization of eucalyptus tar pitches. Energy & Fuels 15, 449-454.

Purevsuren, B., Avid, B., Gerelmaa, T., Davaajav, Y., Morgan, T.J., Herod, A.A., Kandiyoti, B. (2004). The characterization of tar from pyrolysis of animal bones. Fuel 83, 799-805.

Qin, Y.H., Feng, J., Li, W.I. (2010). Formation of tar and its characterization during air-steam gasification of sawdust in a fluidized bed reactor. Fuel 89, 1344-1347.

Radasch, A.H. (1937). Distillation of coal tar. (United States patent number 2,066,386).

Raje, N., Darshana, A.A., Reddy, A.V.R. (2009). Compositional Characterization of carbon electrode material: A study using simultaneous TG-DTA-FTIR. Thermochimica Acta 496, 143-150.

Rocha, J.D., Coutinho, A.R., Luengo., C.A. (2002). Biopitch produced form eucalyptus wood pyrolysis liquids as a renewable binder for carbon electrode manufacture. Journal of Brazilian Chemical Engineering 19 (2) 127-132.

Salvatore, J. R. (2003). Manual on significance of tests for petroleum products, West Conshohocken, PA: ASTM International, 7th Edition Chapter 8.

Sato, S., Sato, K., Imamura, Y., Kon, J. (1975). Determination of the thermal shock resistance of graphite by arc discharge heating. Carbon 13 (4), 309-316.

Sem, M.O. (1954). The Söderberg self-baking electrode. Journal of Electrochemical Society 101 (10), 487-492.

Shoko, L., Beukes, J.P., Strydom, C.A. (2013). Determining the baking isotherm temperature of Söderberg electrodes and associated structural changes. Minerals Engineering 49, 33-39.

Snape, E.S., Kenwright, A.M., Bermejo, J., Fernandez, J., Moinelo, R.S. (1989). Evaluation of the aromatic structure of coal tar pitch by solid and solution state n.m.r. Fuel 68 (12), 1605-1608.

Solum, M.S., Pugmire, R.J., Grant D.M. (1989). ^{13}C Solid-State NMR of Argonnne premium coals. Energy & Fuels 3, 187-193.

Speight, J.G. (1998). The chemistry and technology of petroleum, Marcel Dekker publishers, 3rd edition, 29-31.

Speight, J.G. (2005). Handbook of coal analysis. John Wiley & Sons, Inc., Publication

Stadelhofer, J., Frank, G.H., Kohler, H., Louis, H. (1982). Process for the production of high grade carbonaceous binders. (United States patent number 4, 339, 328, 13).

Stiller, A.H., Zondlo, J.W., Stanberry P.G. (1998). High purity isotropic graphite from coal (United States patent number 5, 705,139 6).

Strydom, C.A., Bunt, J.R., Schobert, H.H., Raghoo. (2011). Changes to the functional groups of an inertinite rich medium rank bituminous coal during acid treatment processes. Fuel Processing Technology 92, 764-770.

Stuart, B. (1996). Modern Infrared spectroscopy. John Wiley and Sons, New York. pp. 19-31

Takagi, H., Maruyama, K., Yosizawa, N., Yamada, Y., Sato, Y. (2004). XRD analysis of carbon stacking structure in coal during heat treatment 83, 2427-2433.

Takashi, H., Kawamoto, H., Saka, S. (2008). Secondary reactions of lignin derived tar components. Journal of analytical and applied pyrolysis 83, 78-87.

Tiwari, K.K., Das, P.D., Ghosh, K.A., Ghosh, K.T., Dumka, C.U., Ghosh, S.N. (1998). Processing of by-products from carbonization of non-caking coals; recovery of tar acids. Fuel processing technology 57, 131-147.

Toromanhoff, I., Habashi, F. (1990). Historical metallurgy notes, Carl Wilhelm Söderberg. The metallurgical society 82, 90-92.

Tucker, K.W. (1981). Use of Chloro-hydrocarbons to produce high density electrodes. (United States patent number 4,308,177).

Van Niekerk, D., Pugmire, R.J., Solum, M.S., Painter, O.C., Mathews, J.P. (2008). Structural characterization of vitrinite-rich and inertnite-rich Permina-aged South African bituminous coals. International Journal of Coal petrology 76, 290- 300.

Visser, M. (2006). An overview of the history and current operational facilities of Samancor chrome. South African pyrometallurgy, 285-293.

Walker, P.L, JR. (1986). Coal derived carbons. Carbon 24 (4) 379-386.

Watt, M., Fletcher, T.H., Solum, M.S., Pugmire, R.J. (1996). Chemical structure of coal tar during devolatilization, Twenty-Sixth Symposium (International) on Combustion/The Combustion Institute, 1996/pp. 3153-3160.

Wissler, M. (2006). Graphite and carbon powders for electrochemical applications. Journal of power sources 156, 142-150.

Multi Linear Regression. www.stat.yale.edu/Courses/1997-98/101/linmult.htm (Date accessed: 29 April 2013).

Yarushina, T.V., Akbashev, V.A., Plyukhin, V.A., Akbashev, M.A., Gyrlya, I.M., Parshikov, A.N. (2007). Pericalse-carbon composite refractories with a new complex binder. Refractories and industrial ceramics 48 (3), 170-175.

Yu, B., Wang, C., Chen, M., Zheng, J., Qi, J. (2012). Two-step chemical conversion of coal pitch to isotropic spinnable pitch. Fuel Processing Technology 104, 155-159.

Yu, Q., Brage, C., Chen, G., Sjostrom, K. (1997). Temperature impact on the formation of tar from biomass pyrolysis in a free-fall reactor. Journal of Analytical and Applied Pyrolysis 40-41, 481-489.

Yue, C., Watkinson, A.P (1998). Pyrolysis of pitch. Fuel 77 (7), 695-711.

Yue-ying W., Jie-jun, L., Jie, X., Chen-jia, J., De-qing W., Wei-Zhong, D. (2010). Determination of the volatile fraction of coal tar. Journal of Shanghai University (English Edition) 15 (5), 313-321.

Zander, M. (1987). On the composition of pitches. Fuel 66, 1536-1539.

Zander, M. (1987). Recent advances in pitch characterization. Fuel 66, 1459-1466.

Zou, L., Huang, B., Huang, Y., Huang, Q., Wang, C. (2003). An investigation of heterogeneity of the degree of graphitization in carbon-carbon composites. Materials Chemistry and Physics 82, 654-662.

Appendix A

Fundamental properties of CTP samples

Table A1.1 Determination of SP

Sample identity	SP 1 (°C)	SP 2 (°C)	Average SP (°C)
CTP 1	122.1	121.7	121.2
CTP 2	81.8	81.9	81.9
CTP 3	66.6	66.4	66.5
CTP 4	93.9	94.1	94.0
CTP 5	94.1	95.0	94.6
CTP 6	66.6	64.5	65.6
CTP 7	82.3	82.8	82.6
CTP 8	134.8	133.5	134.2
CTP 9	83.7	82.4	83.1
CTP 10	93.5	94.1	93.8
CTP 11	64.4	66.3	65.4
CTP 12	85.0	84.9	85.5

Table A1.2 Determination of coking value (CV)

Sample	Mass of crucible (g)	Mass of crucible + sample (g)	Mass of sample (g)	Mass of crucible + residue(g)	Mass of residue (g)	% Coking value
CTP 1	20.3149	23.3155	3.0006	22.0235	1.7086	56.9
CTP 2	17.0878	20.0891	3.0013	18.2019	1.1141	37.1
CTP 3	20.8260	23.8270	3.0010	21.9431	1.1171	37.2
CTP 4	17.1349	20.1361	3.0012	18.5390	1.4041	46.7
CTP 5	20.8259	23.8263	3.0004	22.2503	1.4244	47.4
CTP 6	20.3154	23.3156	3.0002	21.5603	1.2449	41.5
CTP 7	17.6597	20.6607	3.0010	19.0876	1.4279	47.5
CTP 8	21.1928	24.1950	3.0022	23.0029	1.8101	60.3
CTP 9	21.1929	24.1949	3.0020	22.4827	1.2898	42.9
CTP 10	17.0876	20.0885	3.0009	18.5837	1.4961	50.0
CTP 11	17.6589	20.6600	3.0011	19.0580	1.3991	46.6
CTP 12	20.8400	23.8417	3.0017	22.3021	1.4621	48.7

Table A1. 3 Determination of quinoline insolubles (QI)

Sample identity	Mass of sample (g)	Mass of celite powder (g)	Mass of crucible + celite powder (g)	Mass of crucible + residue (g)	Mass of residue (g)	% Quinoline insoluble
CTP 1	0.5021	0.50004	67.9754	65.5088	0.5334	6.6
CTP 2	1.0026	0.50002	66.8613	67.3977	0.5364	3.6
CTP 3	1.0038	0.50004	69.3638	69.9010	0.5372	3.7
CTP 4	1.0017	0.50004	69.2093	69.7544	0.5451	4.5
CTP 5	1.0003	0.50002	67.9076	68.4540	0.5464	4.6
CTP 6	1.0049	0.50008	66.7560	67.2952	0.5392	3.8
CTP 7	1.0030	0.5012	69.1722	69.7279	0.5557	5.4
CTP 8	0.5006	0.5012	68.7735	69.3136	0.5401	7.0
CTP 9	1.0011	0.5015	68.2286	68.7590	0.5304	2.9
CTP 10	1.0020	0.5008	66.9588	67.5179	0.5591	5.8
CTP 11	1.0009	0.5009	69.2419	69.8158	0.5739	7.3
CTP 12	1.0017	0.5003	69.5343	70.1068	0.5725	7.2

Table A1. 4 Determination of toluene insolubles (TI)

Sample identity	Mass of sample (g)	Mass of alundum thimble (g)	Mass of alundum thimble + residue(g)	Mass of + residue (g)	Toluene insoluble (%)
CTP 1	1.0013	26.6194	26.8828	0.2634	26.3
CTP 2	1.5005	28.2084	28.4480	0.2396	16.0
CTP 3	1.5011	27.2206	27.4648	0.2442	16.2
CTP 4	1.5011	27.0585	27.3580	0.2995	20.0
CTP 5	1.5012	27.3787	27.6649	0.2862	19.1
CTP 6	1.5010	33.8062	34.1058	0.2996	20.0
CTP 7	1.5008	29.0319	29.3918	0.3599	24.0
CTP 8	1.0006	26.9936	27.3393	0.3457	34.6
CTP 9	1.5002	27.7310	27.7310	0.3558	23.7
CTP 10	1.5016	33.7911	34.0651	0.2740	18.2
CTP 11	1.5016	26.9899	27.3266	0.3367	22.2
CTP 12	1.5004	29.0229	29.3709	0.3480	23.2

Characterisation of raw CTP

NMR analysis of raw CTP

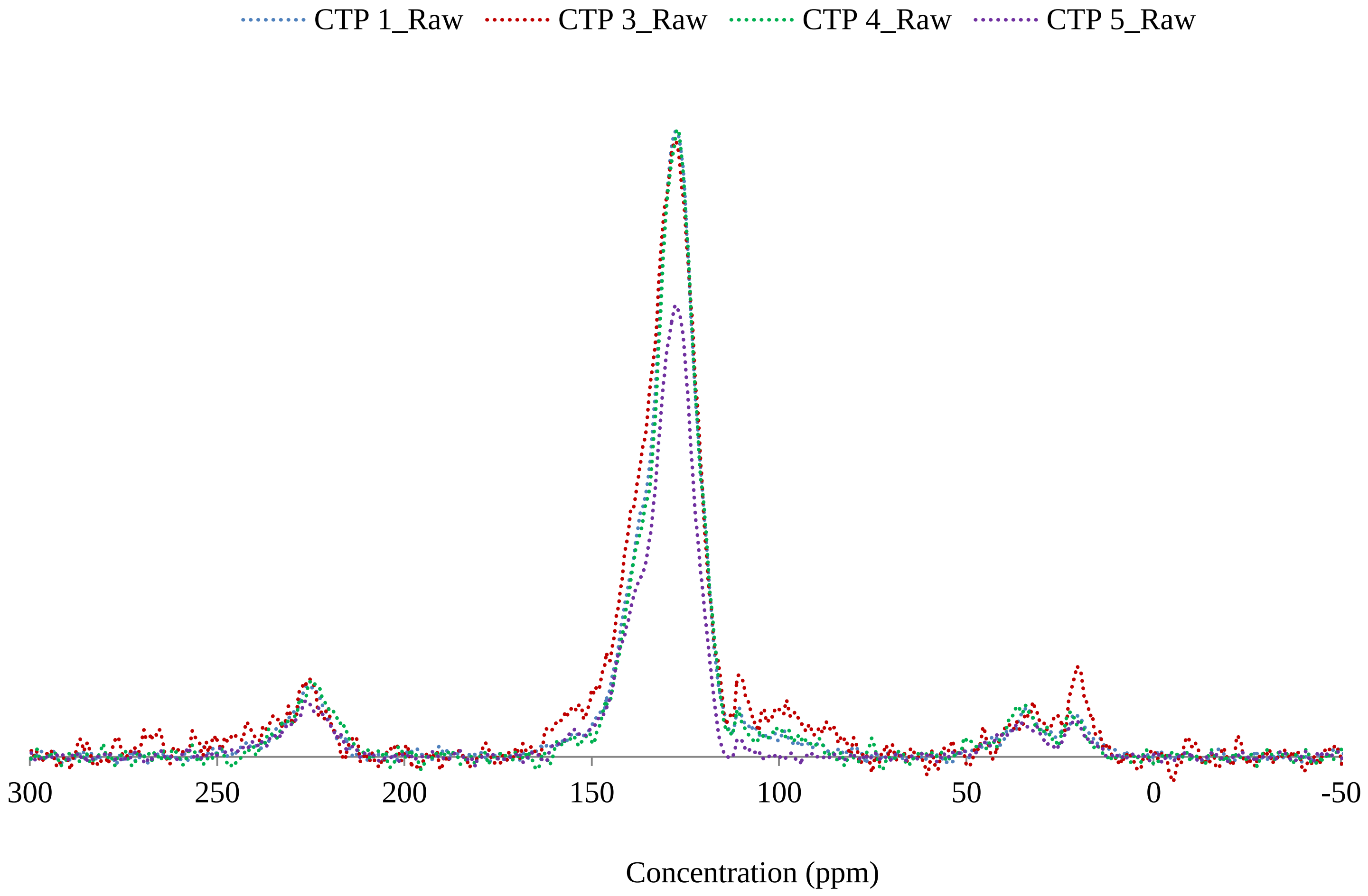

Figure A2.1 Typical CP MAS spectra of as-received CTP samples

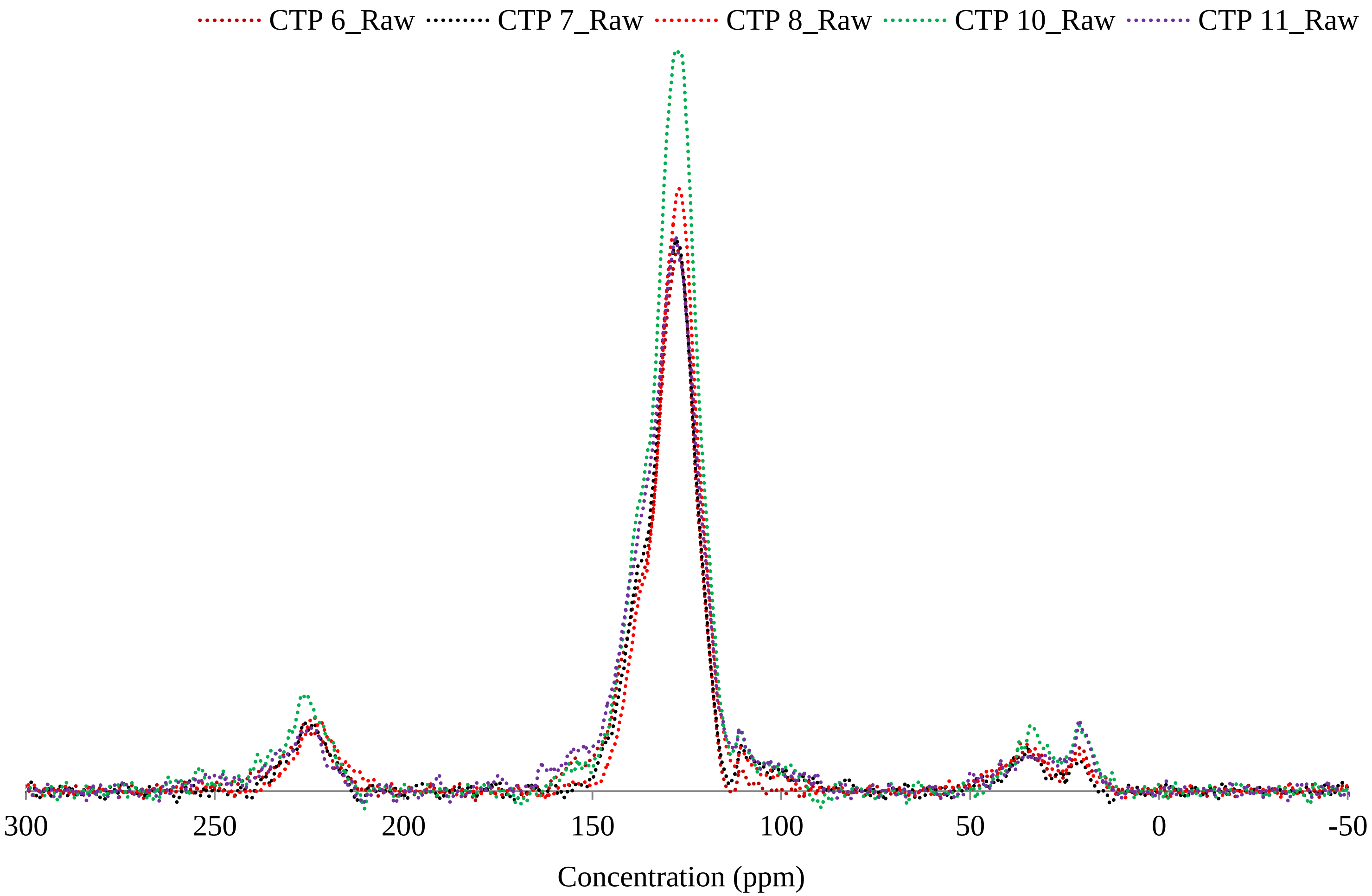

Figure A2.2 Typical CP MAS spectra of as-received CTP samples

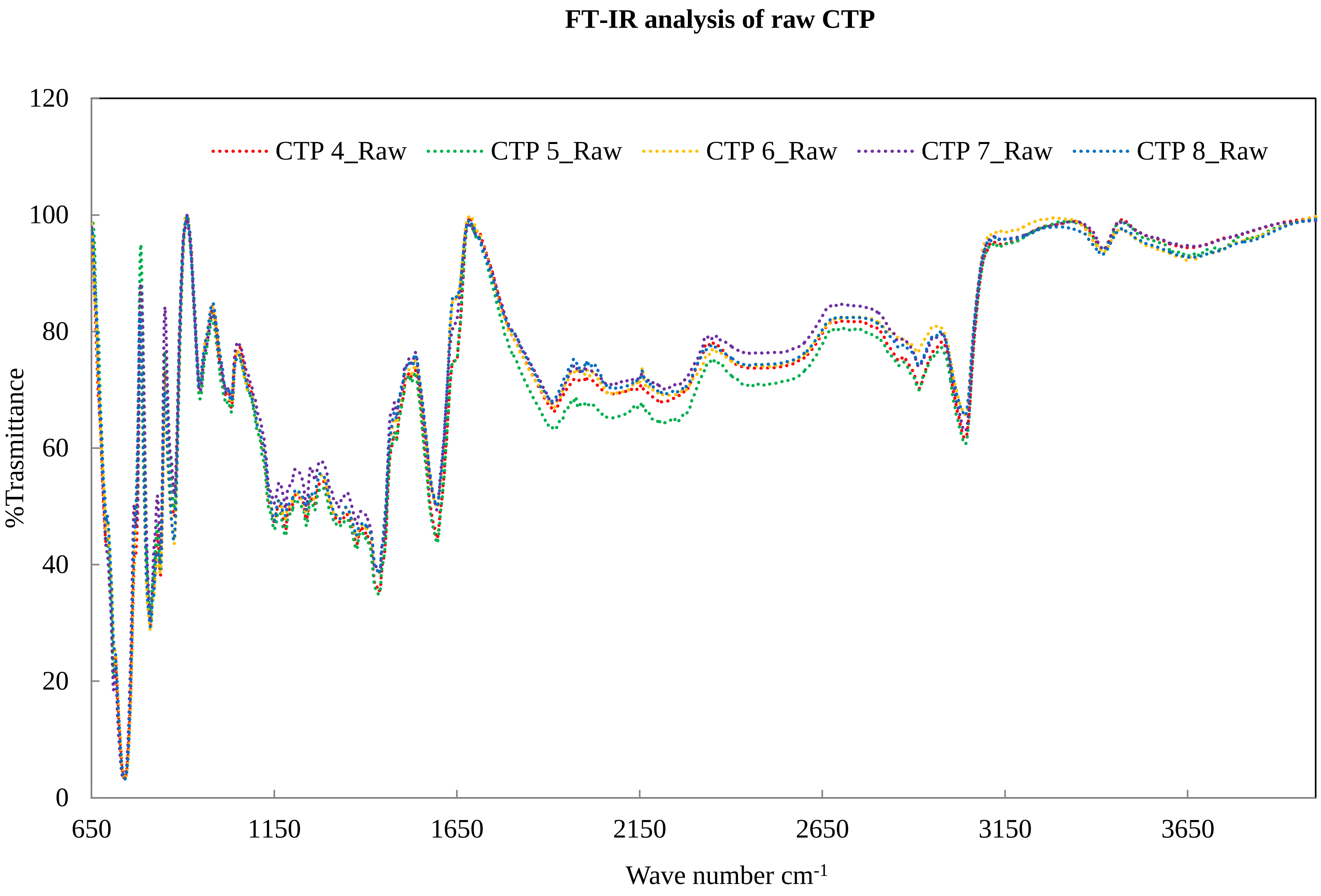

Figure A2.3 FT-IR spectra of raw (as-received) CTP

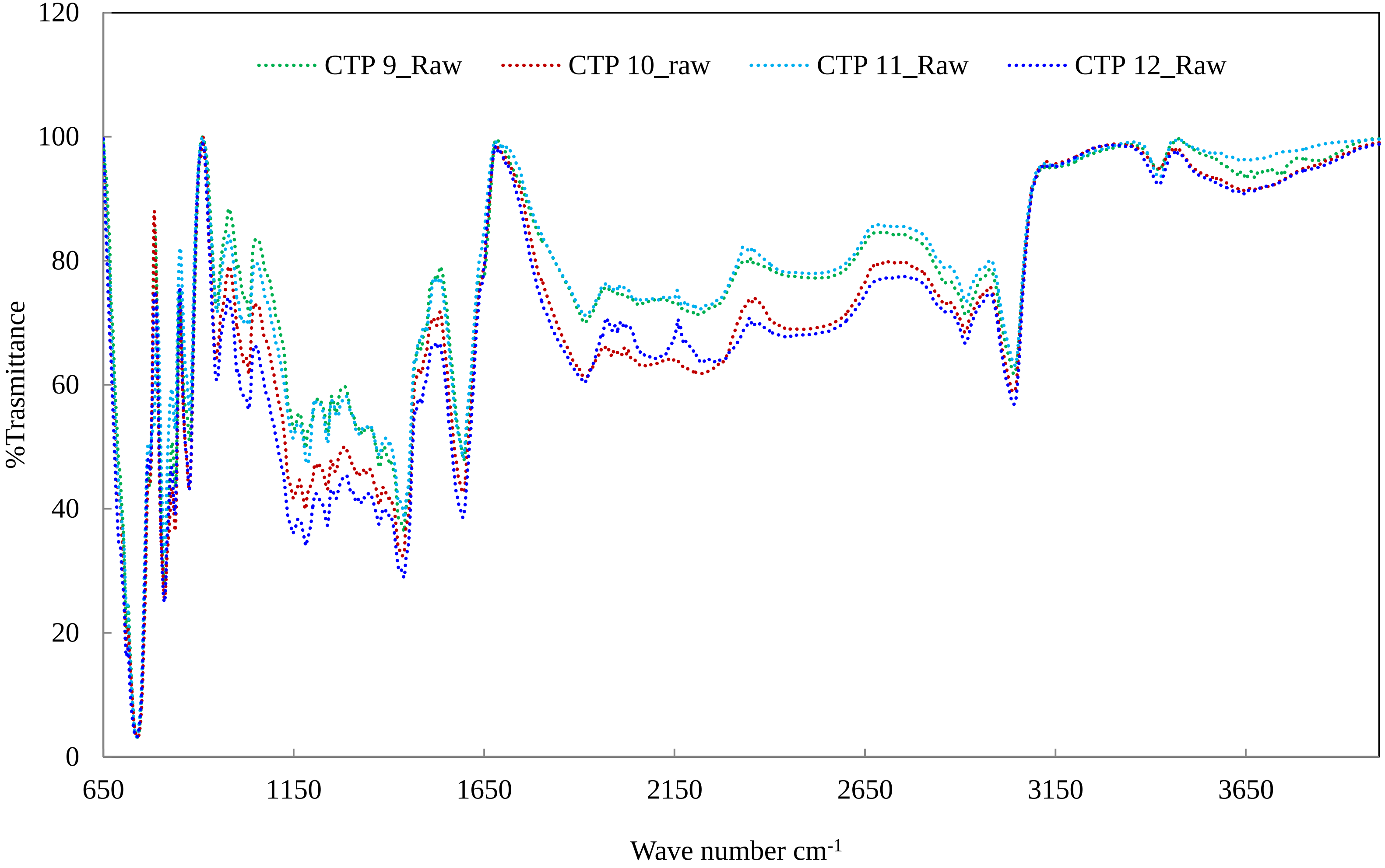

Figure A2.4 FT-IR spectra of raw (as-received) CTP

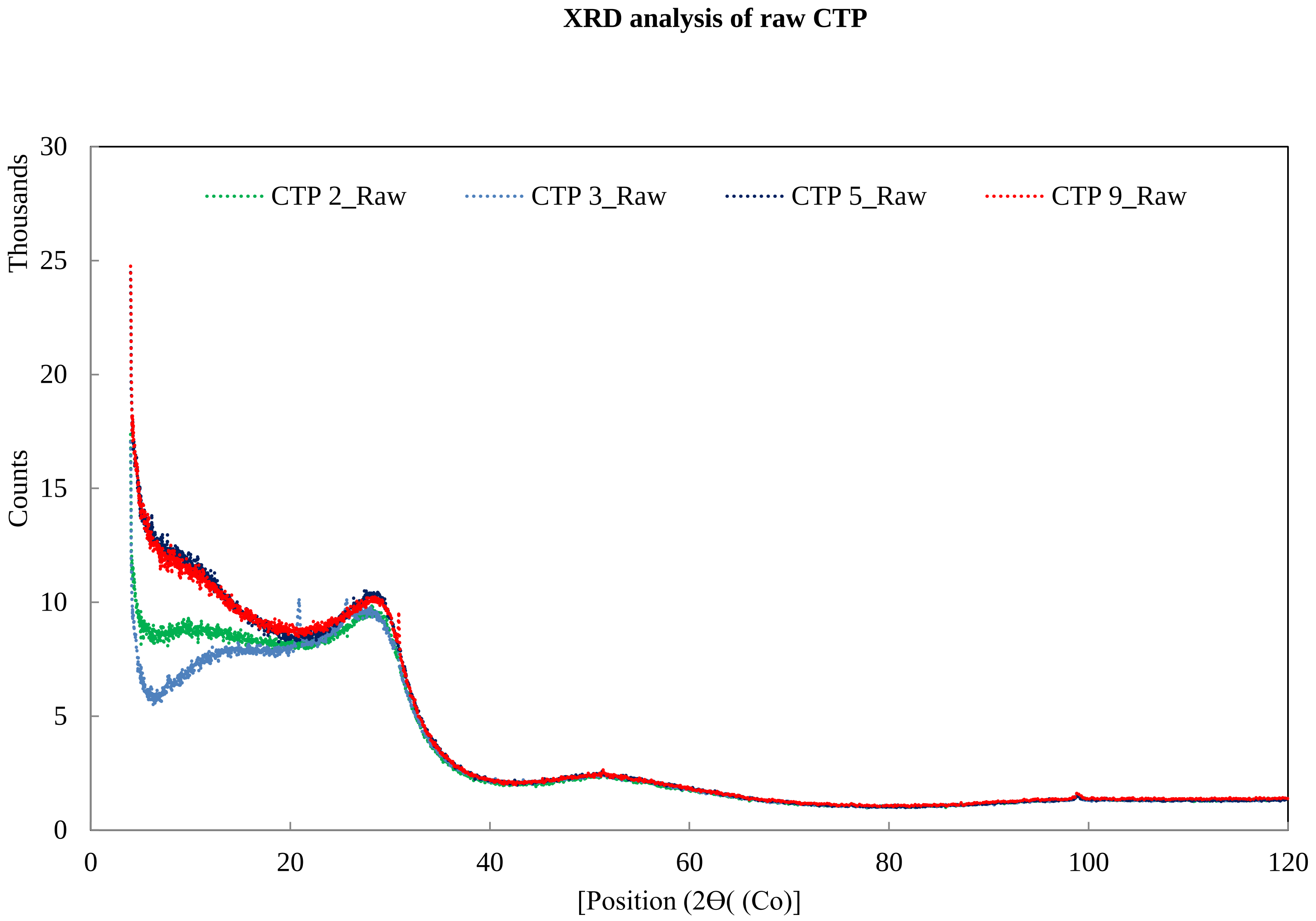

Figure A2.5 XRD diffractograms of raw (as-received) CTP

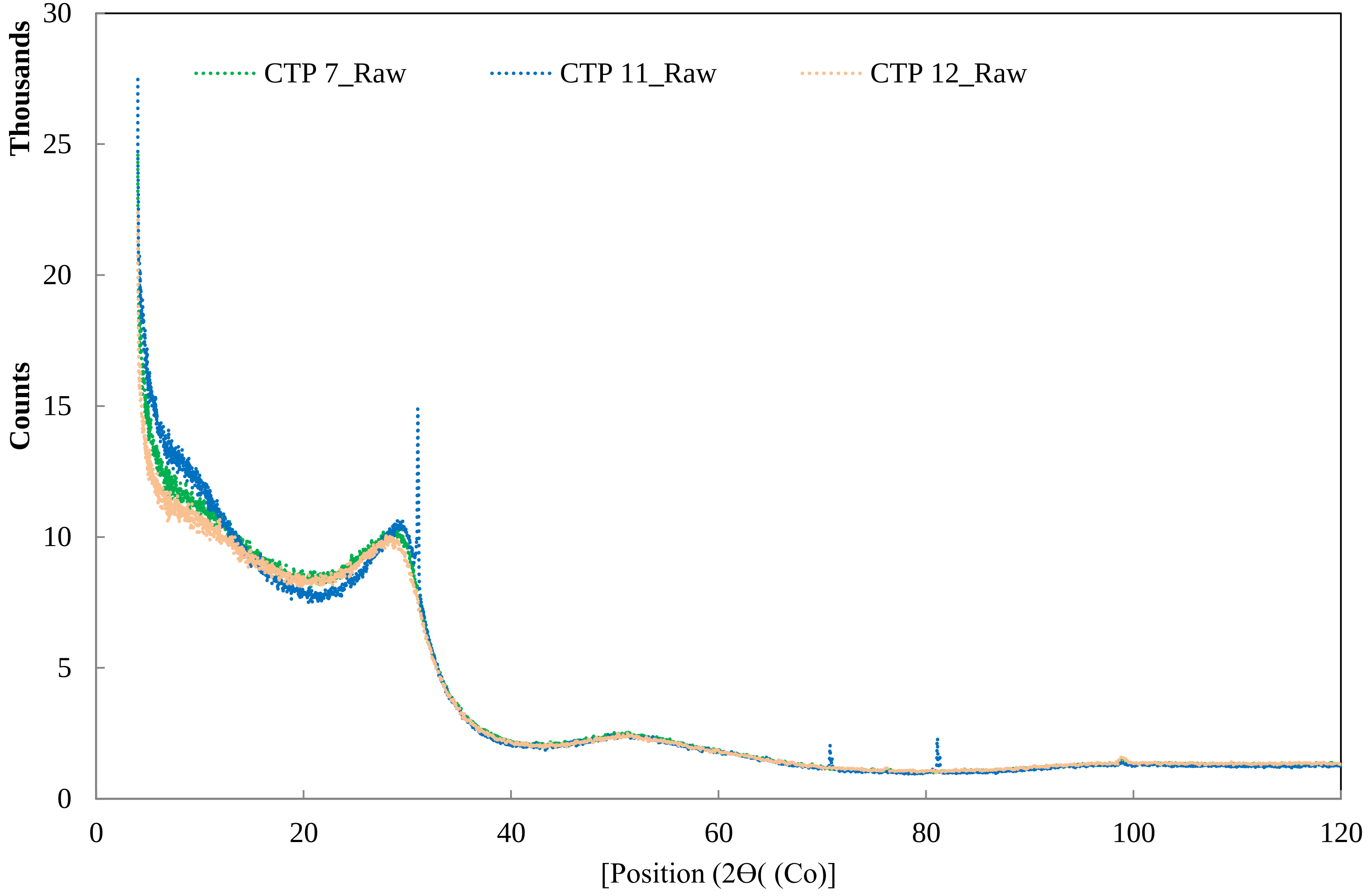

Figure A2.6 XRD diffractograms of raw (as-received) CTP

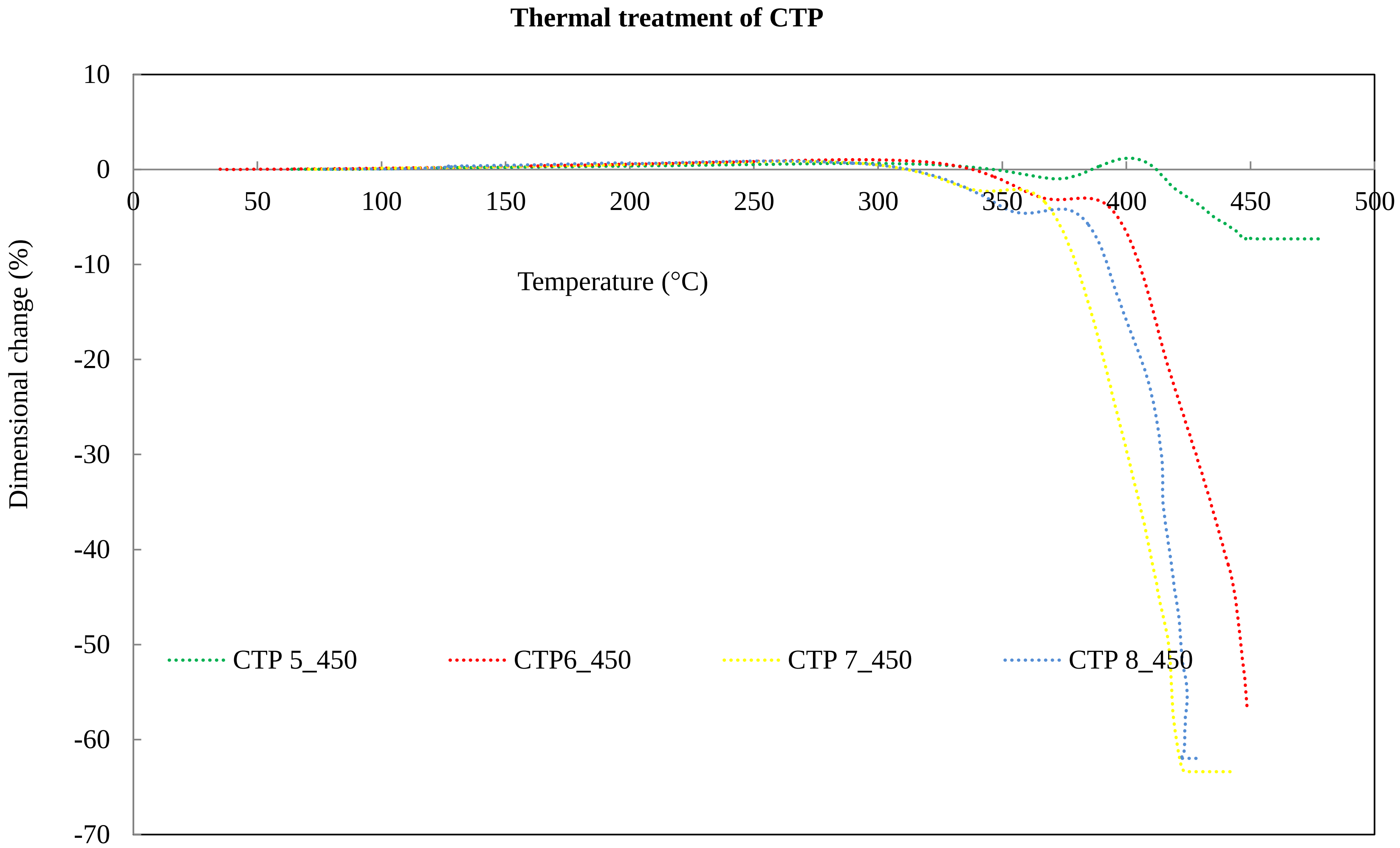

Figure A3.1 Dimensional change patterns of CTP samples pre-treated at 450 °C

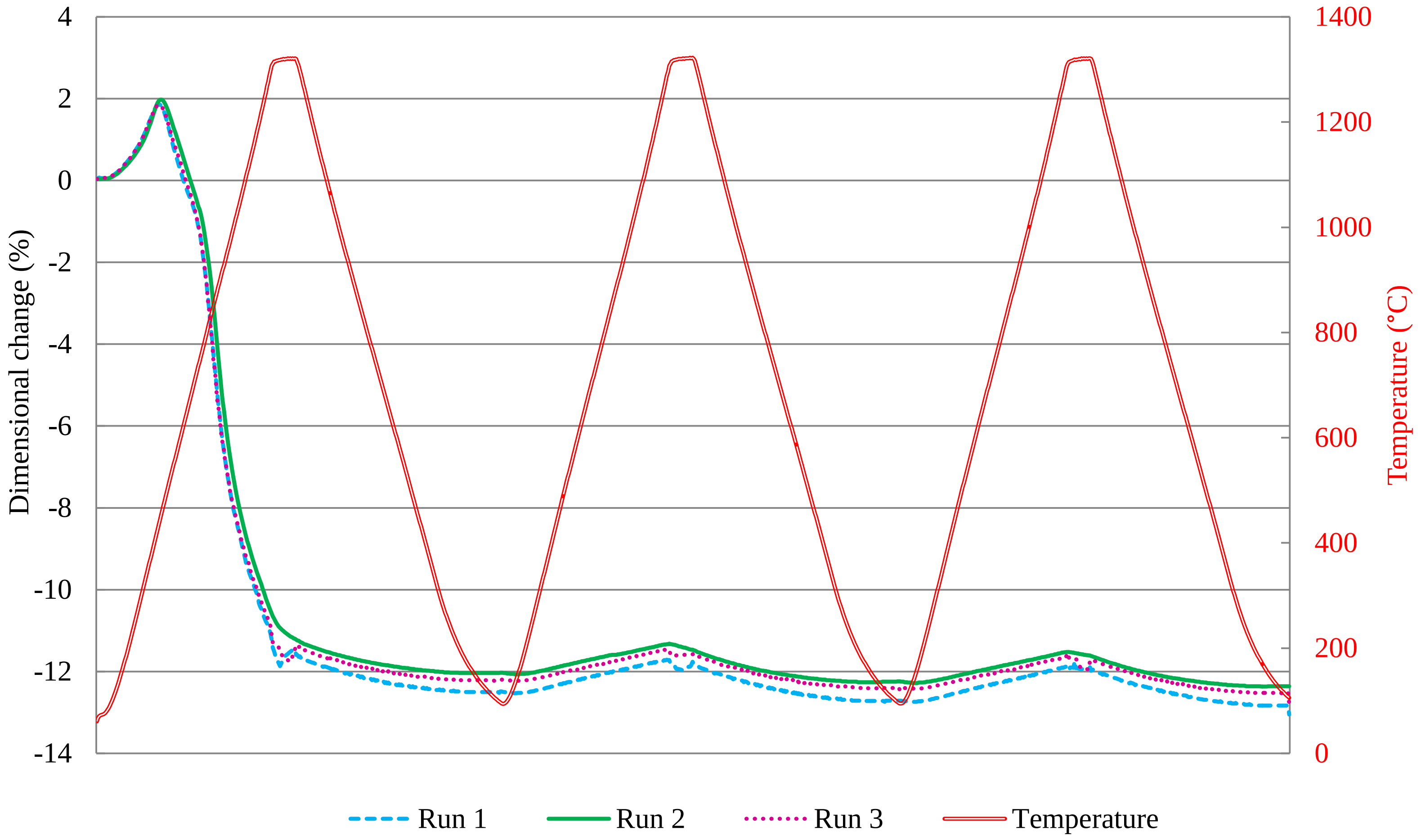

Figure A3.2 TMA behaviour of CTP 2 during three thermal cycles

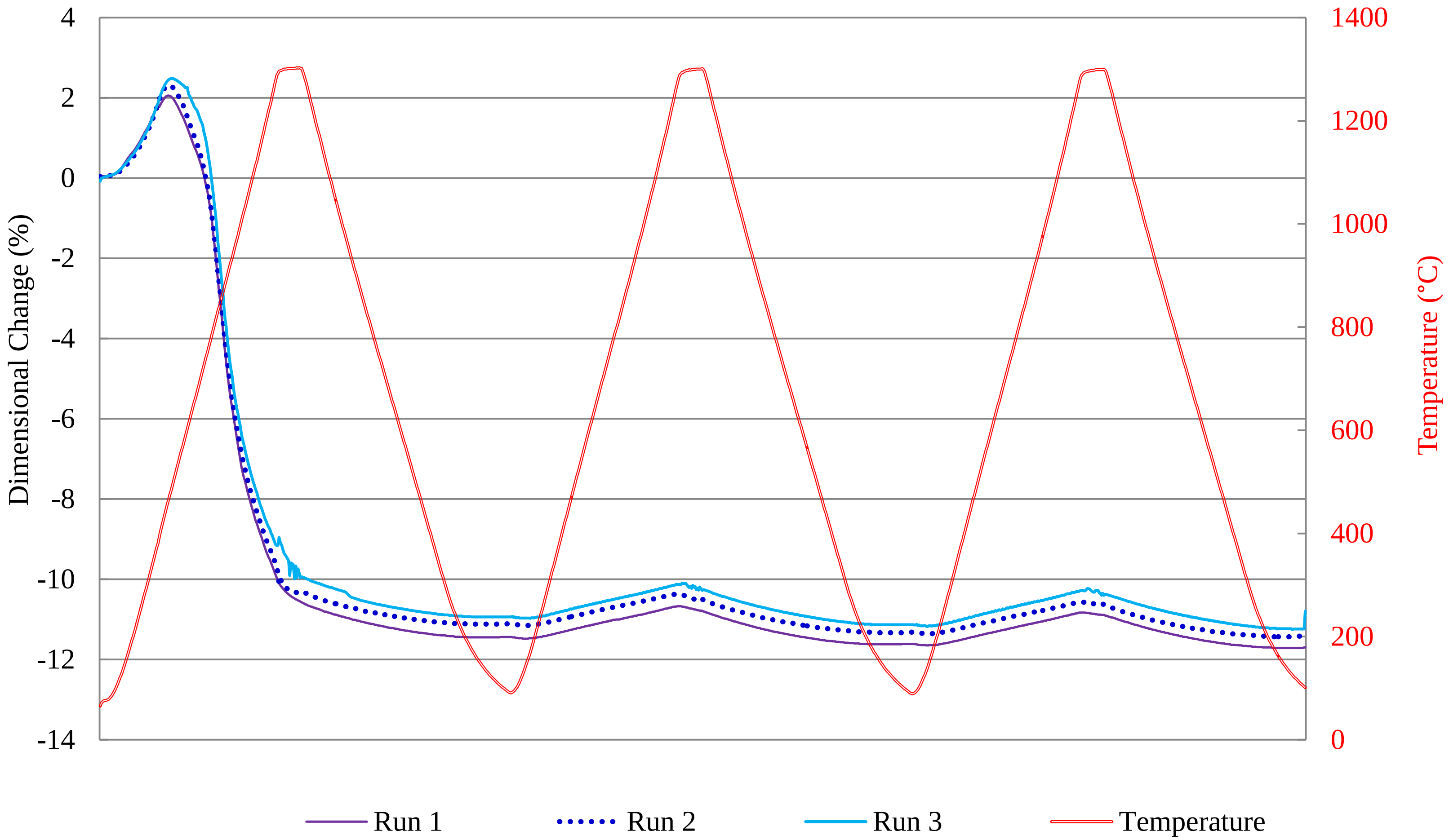

Figure A3.3 TMA behaviour of CTP 3 during three thermal cycles

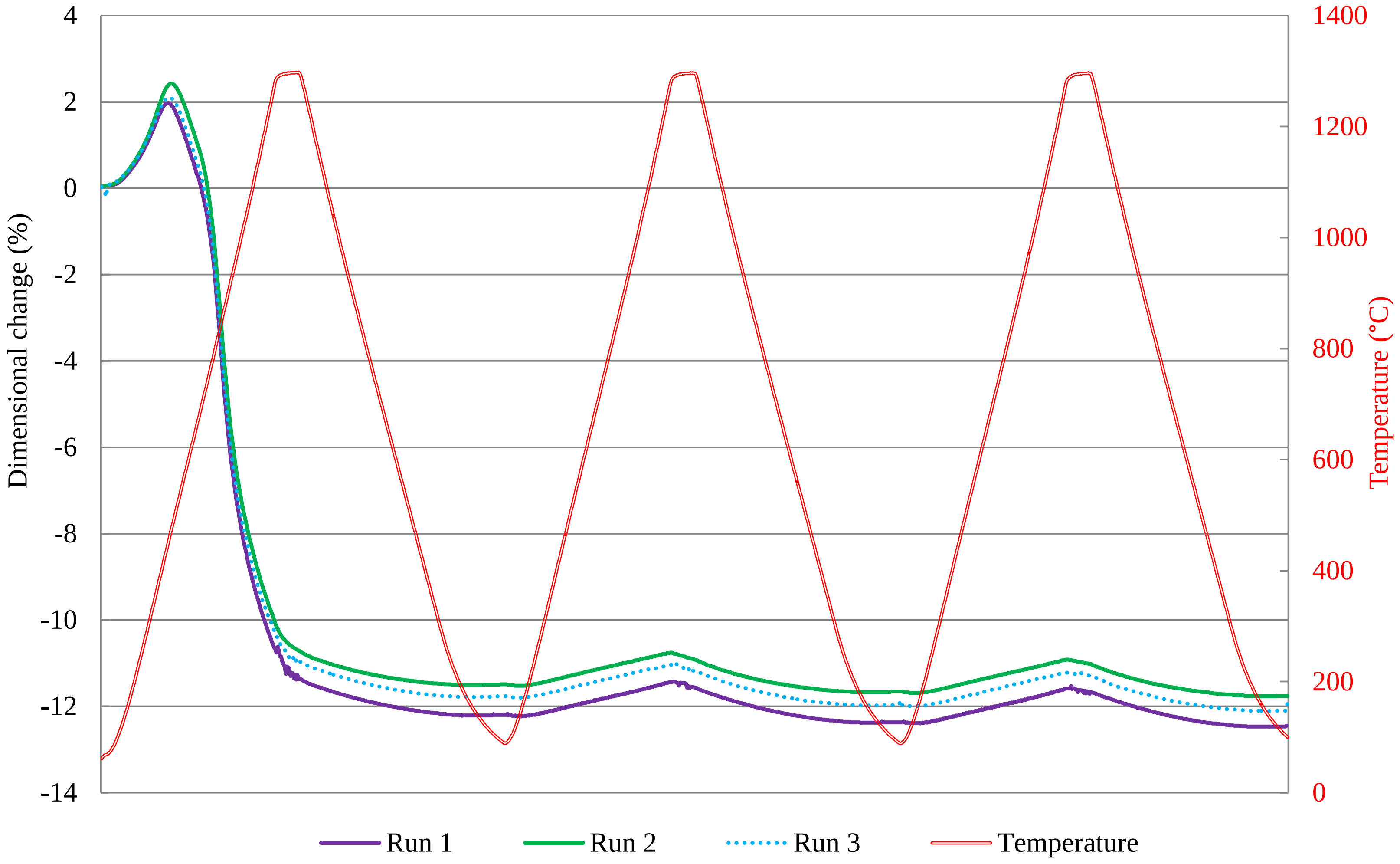

Figure A3.4 TMA behaviour of CTP 5 during three thermal cycles

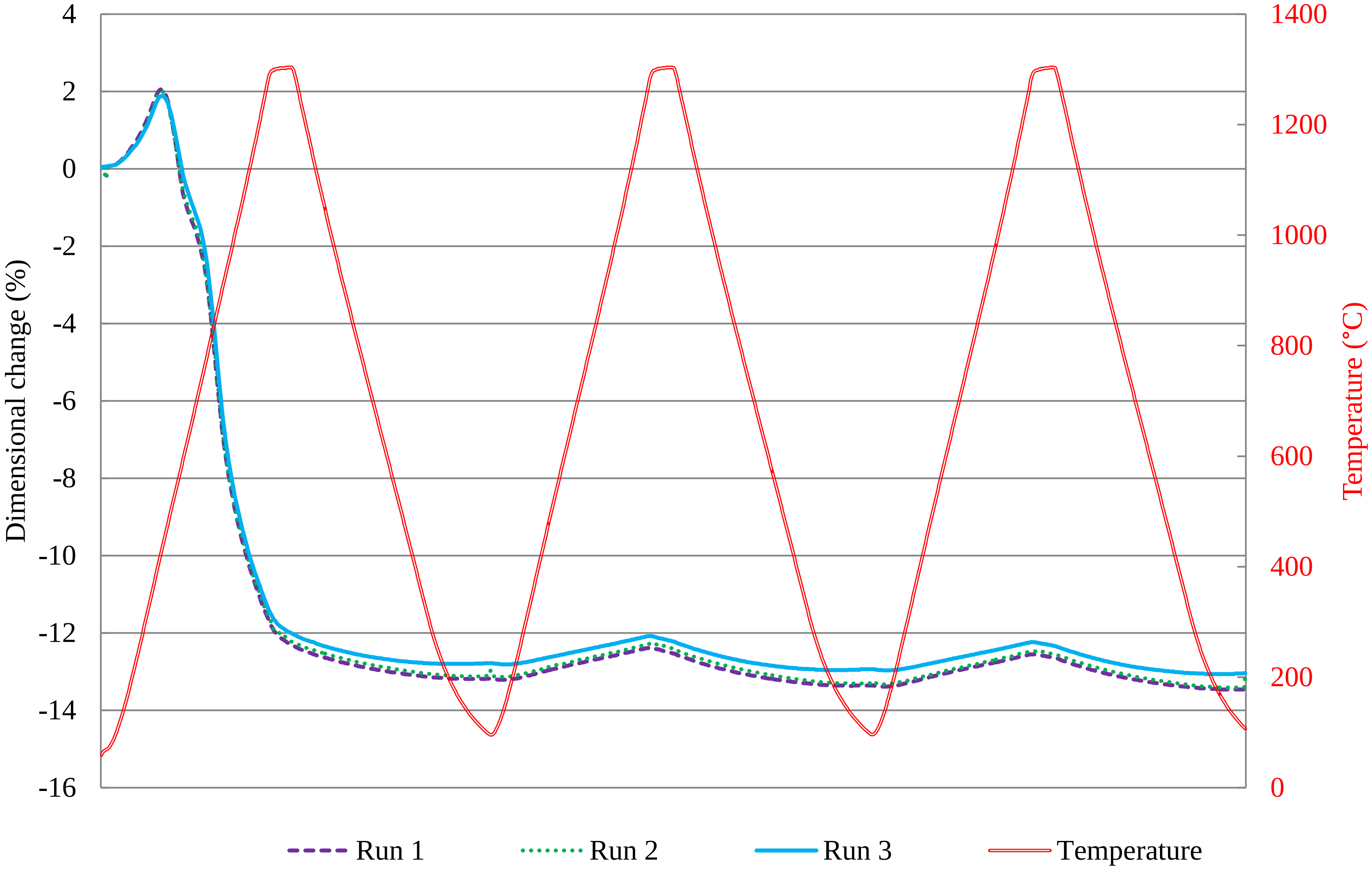

Figure A3.5 TMA behaviour of CTP 6 during three thermal cycles

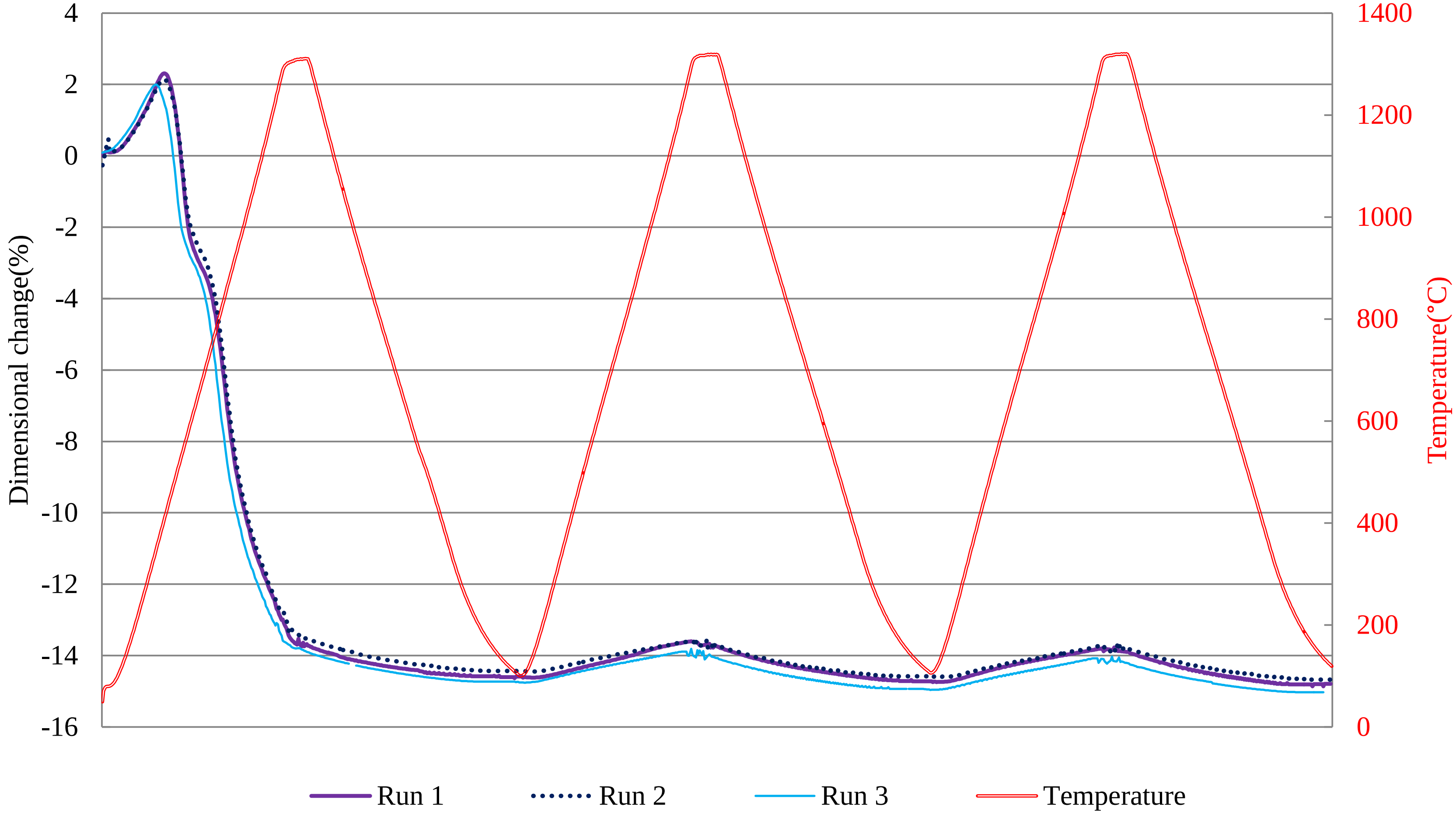

Figure A3.6 TMA behaviour of CTP 8 during three thermal cycles

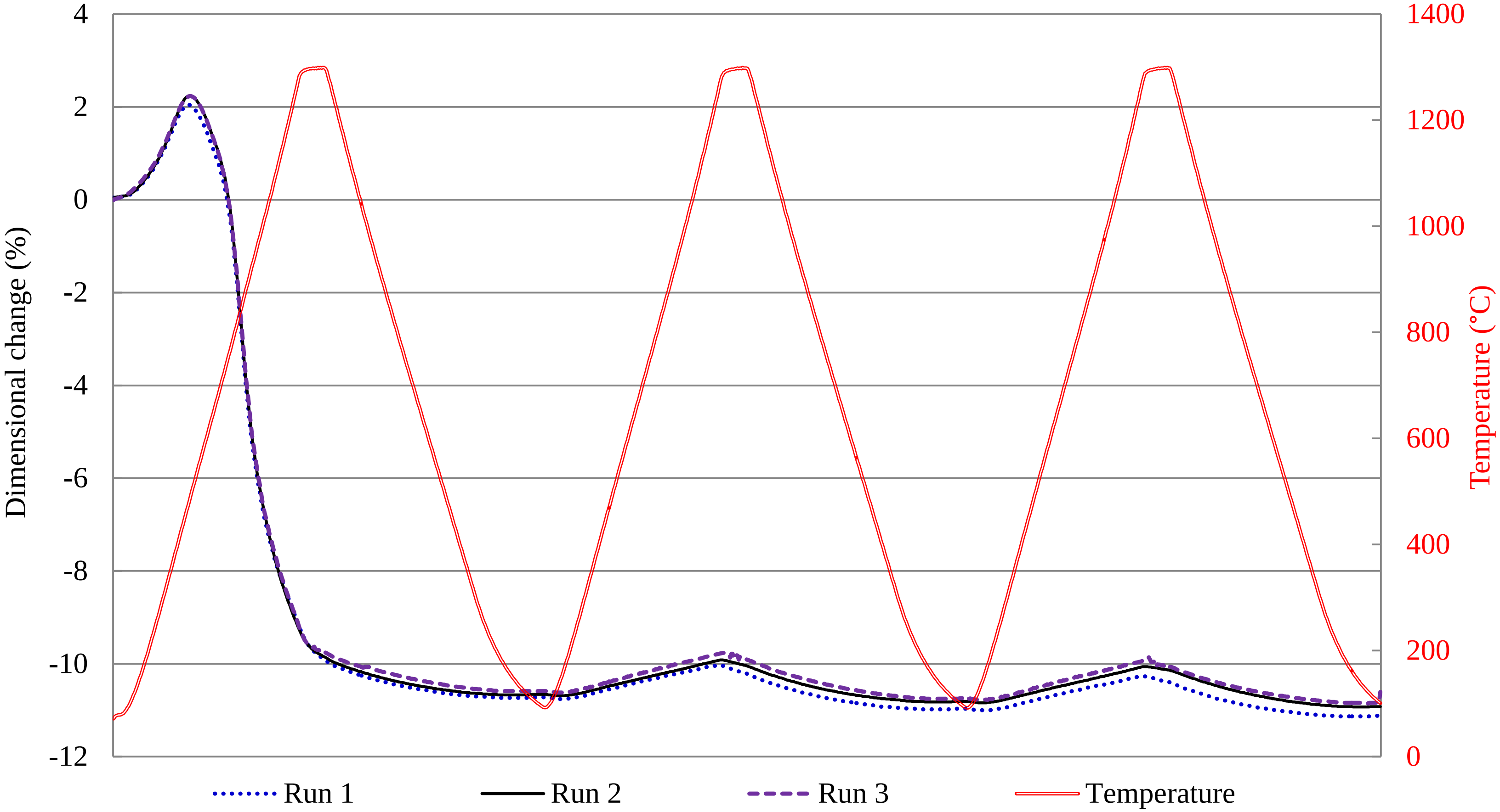

Figure A3.7 TMA behaviour of CTP 10 during three thermal cycles

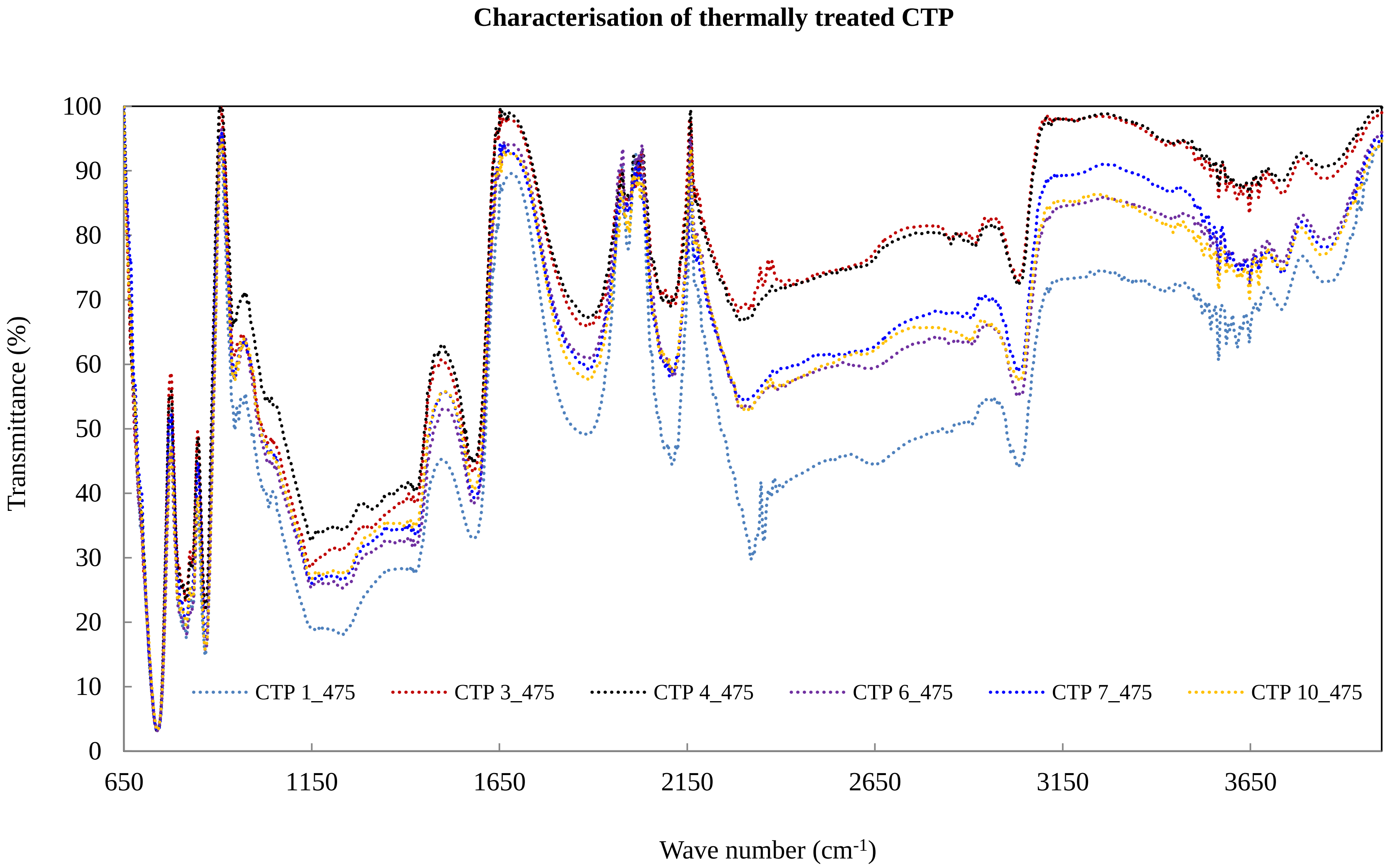

Figure A4.1 FT-IR spectra of CTP thermally pre-treated at 475 °C

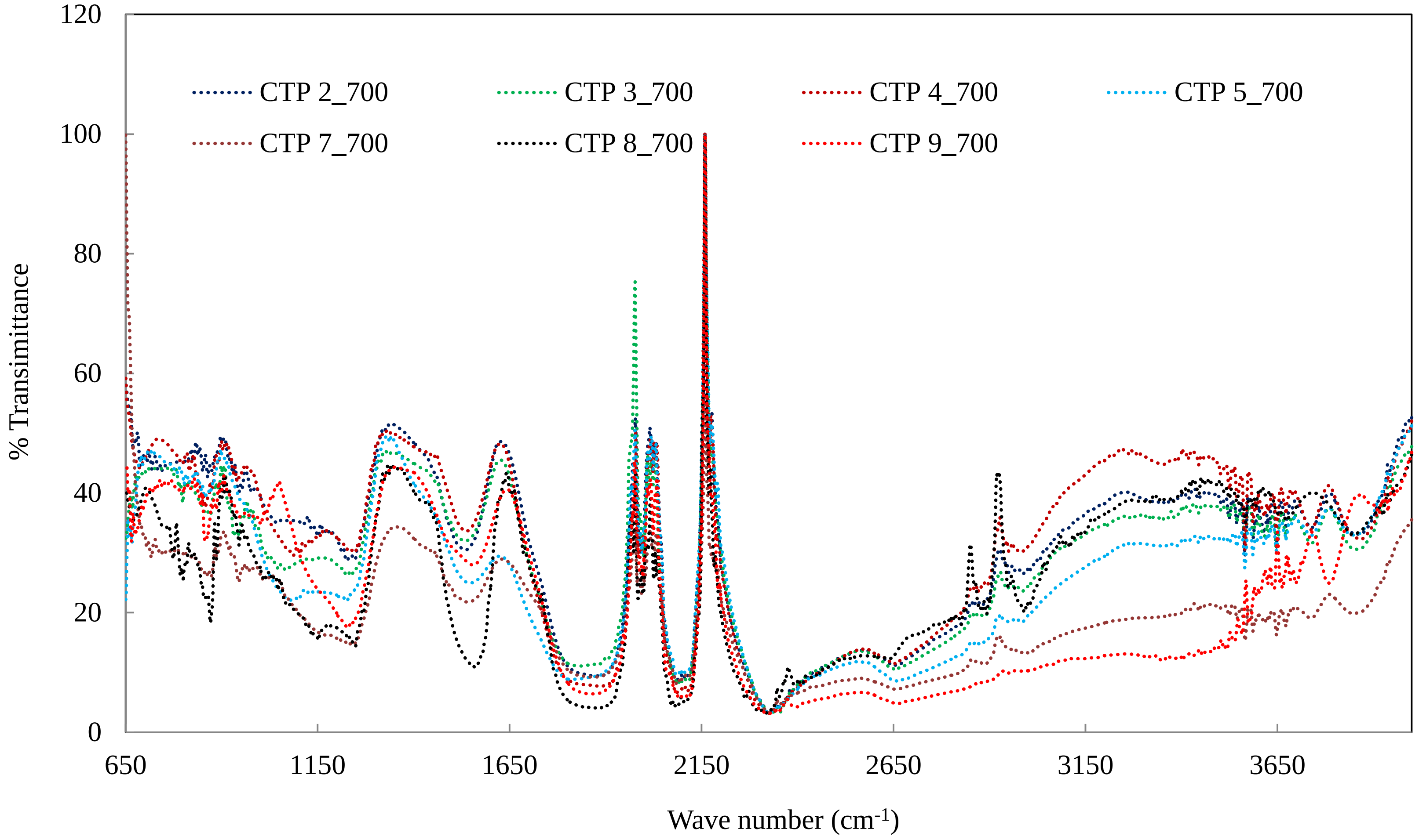

Figure A4.2 FT-IR spectra of CTP thermally treated at 700 °C

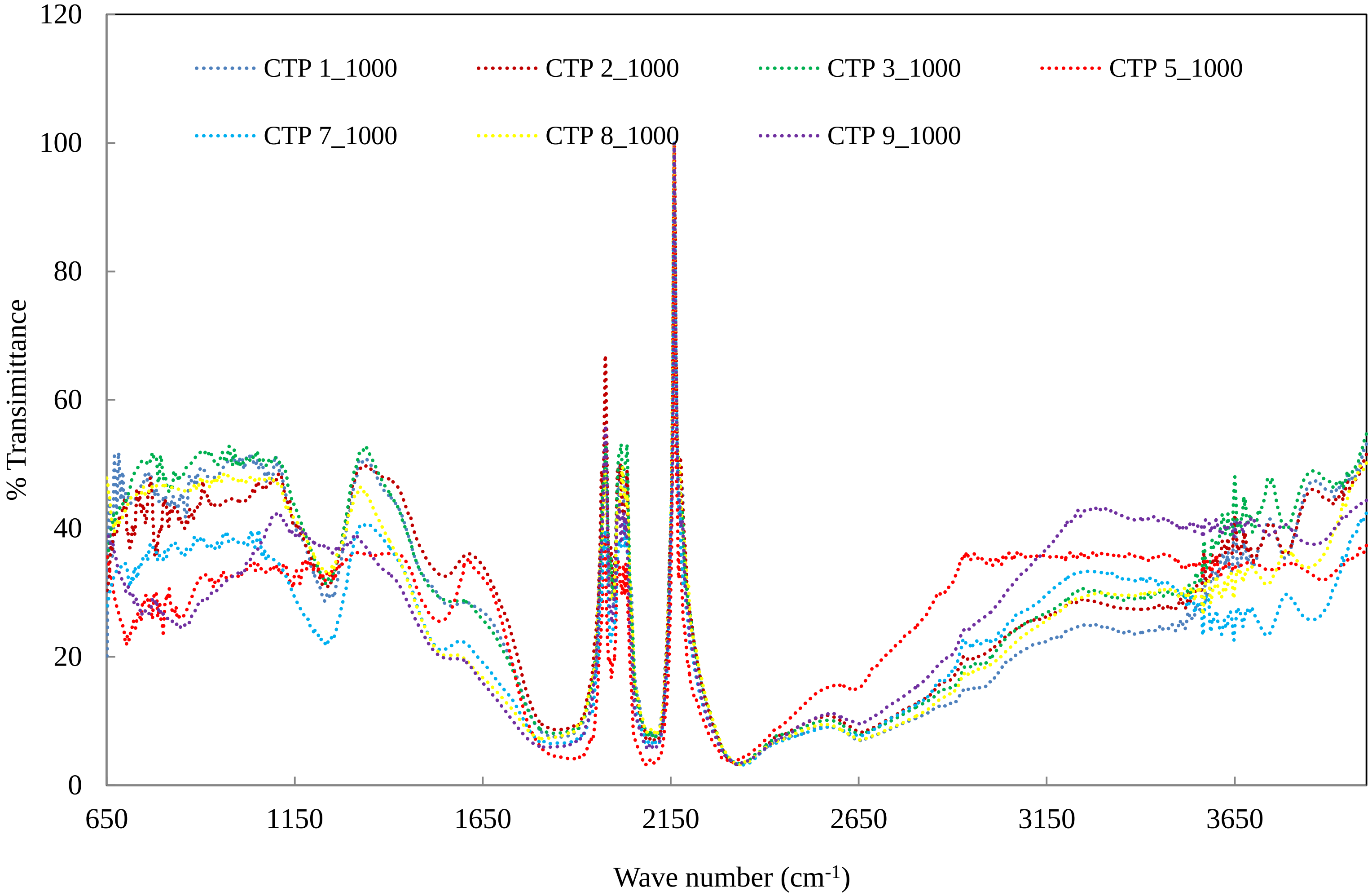

Figure A4.3 FT-IR spectra of CTP thermally treated at 1000 °C

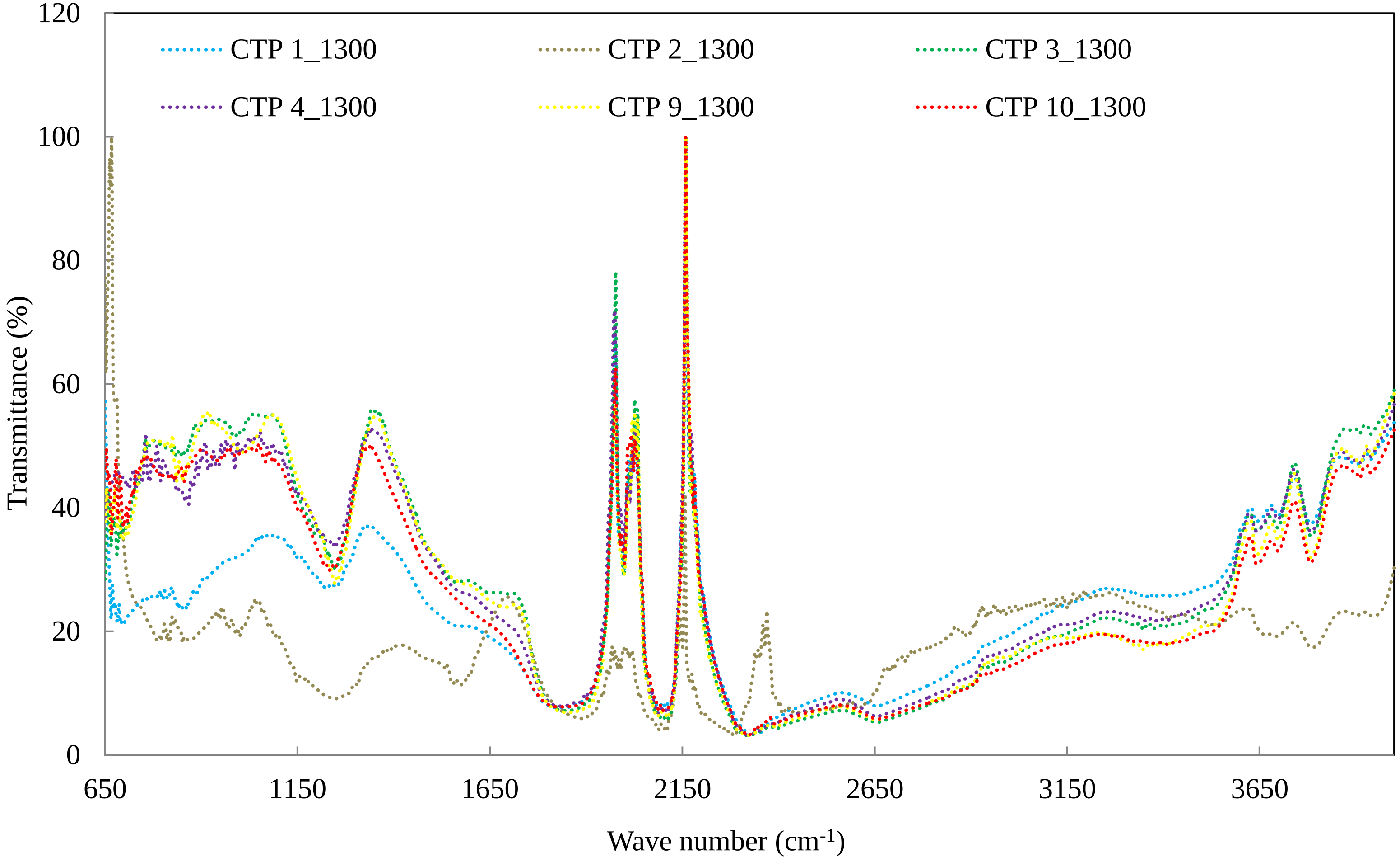

Figure A4.4 FT-IR spectra of CTP thermally treated at 1300 °C

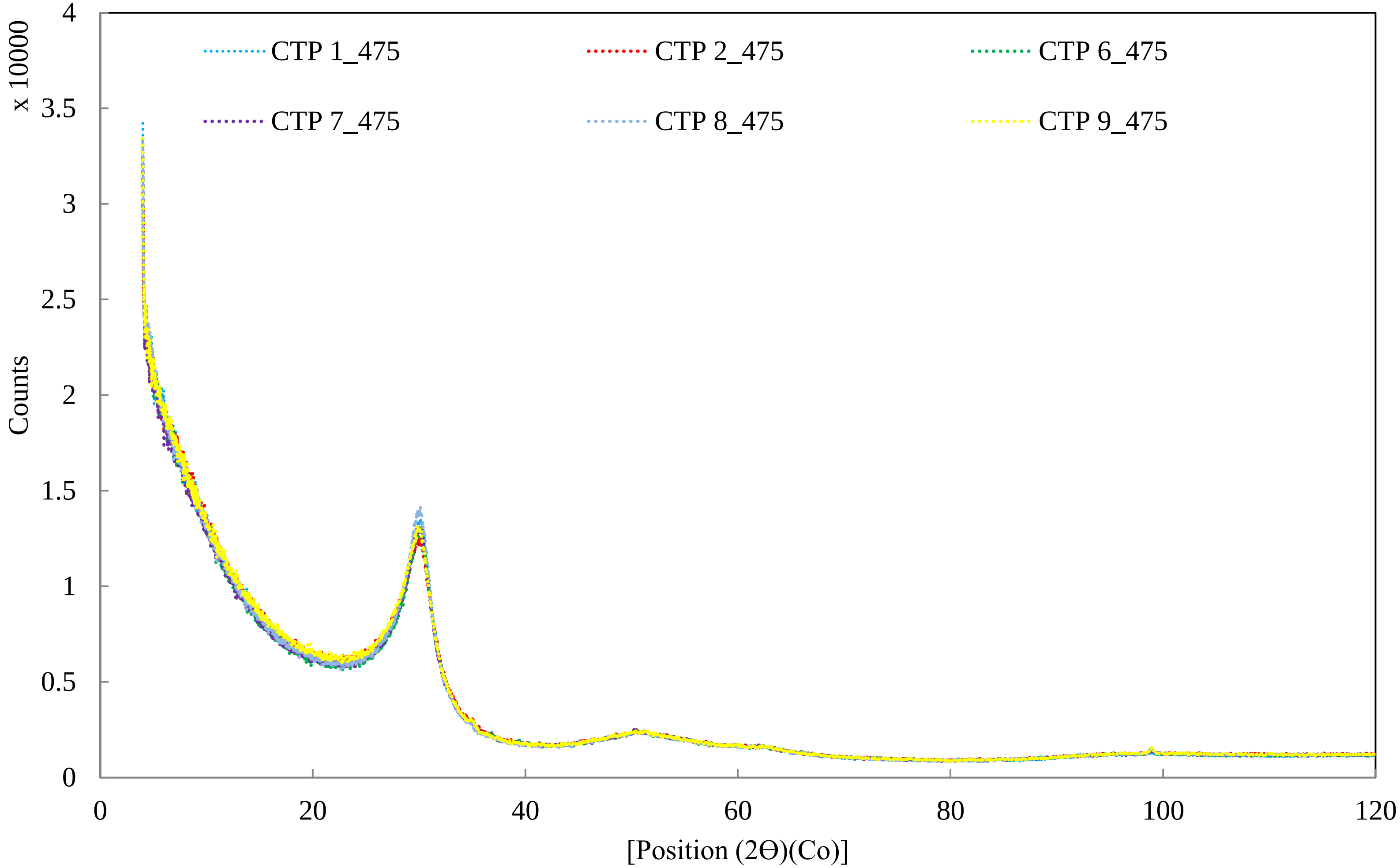

Figure A4.5 XRD diffractograms of CTP thermally treated at 475 °C

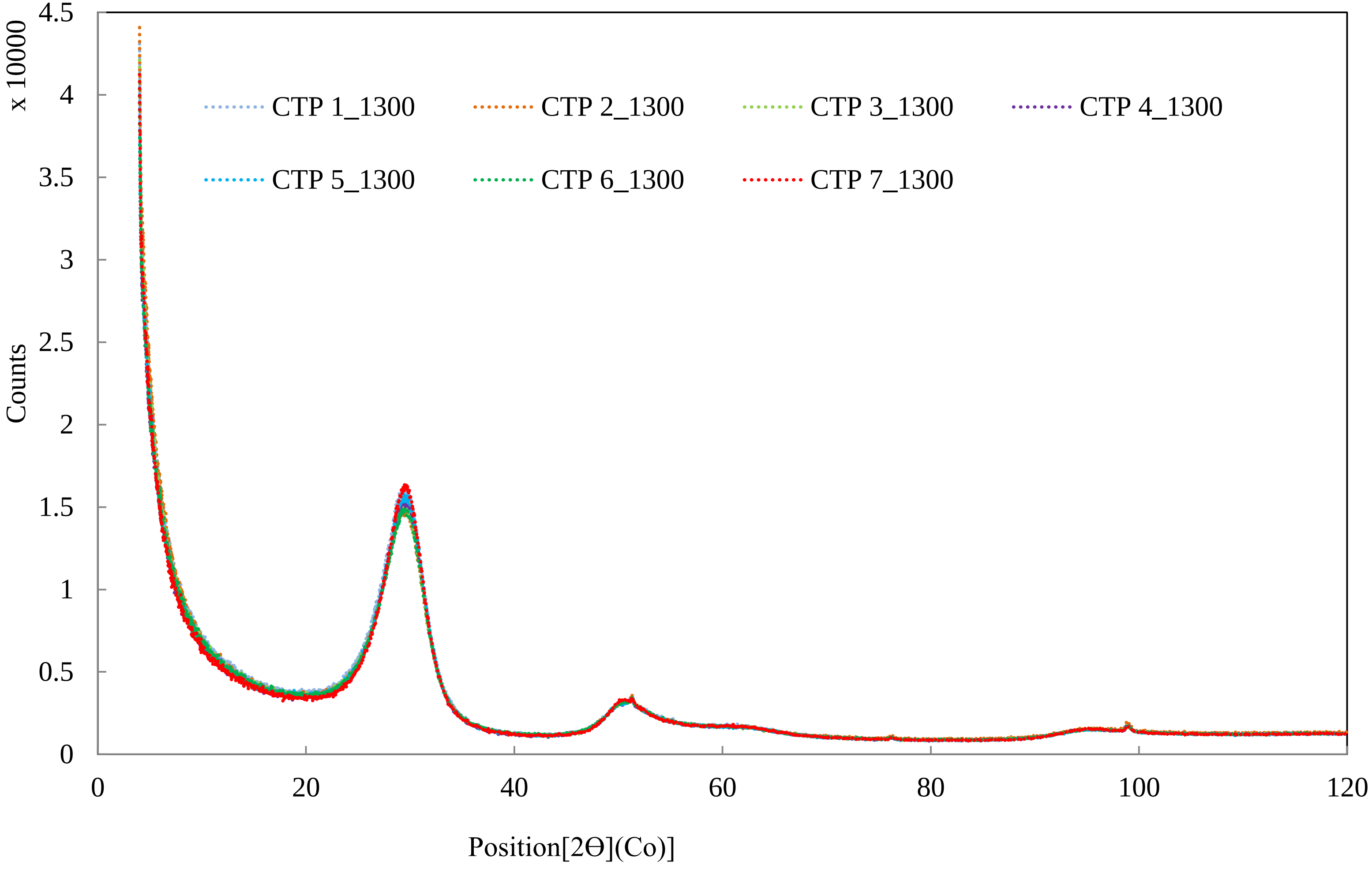

Figure A4.6 XRD diffractograms of CTP thermally treated at 1300 °C

Appendix B
Publications

Minerals Engineering 46–47 (2013) 167–176

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The use of thermomechanical analysis to characterise Söderberg electrode paste raw materials ☆

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ABSTRACT

Continuous self-baking electrodes, i.e. Söderberg electrodes, are commonly employed in the industrial operation of submerged arc furnaces to conduct electrical energy from a transformer(s) to the smelting zone inside the furnace. Söderberg electrodes are formed from Söderberg electrode paste consisting of two components, i.e. a binder that is mostly a coal tar pitch and a solid filler that can be either coke or calcined anthracite. In this paper it is demonstrated how thermomechanical analysis can be used to characterise the thermal dimensional behaviours of Söderberg electrode paste raw materials. Two case study coal tar pitches, three anthracites and a pre-baked graphite electrode sample were characterised. Results indicated that the method applied can be used to determine the baking isotherm temperature more accurately than previously. Enhanced knowledge of the baking isotherm temperature is critical to ensure safe, profitable and continues furnace operation. The results also indicated that the coal tar pitches shrunk approximately 12% if exposed to temperatures above the baking isotherm temperature up to 1300 °C, while the anthracites calcined at 1400 °C expanded 0.6–1.0% in the same temperature range. The magnitude differences in thermal dimensional behaviour and difference in motion (shrinkage *vs.* expansion) indicates the vulnerability of a Söderberg electrode baked for the first time at temperatures exceeding the baking isotherm temperature. In contrast to the calcined anthracites, the uncalcined anthracite samples shrunk 6–8% if exposed to temperatures up to 1300 °C. This stresses the importance of the efficiency of the calcination process of the anthracite prior to Söderberg electrode paste production to enhance dimensional stability of the Söderberg electrode paste. The results also indicated that the method detailed in this paper can be used by Söderberg electrode paste producers to optimise the selection of raw materials and to do quality control on calcined anthracite.

1. Introduction

In the operation of submerged arc furnaces (SAFs) electrodes conduct electrical energy from a transformer(s) to the smelting zone inside the furnace. Generally two types of electrodes systems are used in industrial smelting applications, i.e. pre-baked electrodes and continuous self-baking electrodes (Söderberg electrodes). The Söderberg electrode system is quite commonly applied since Söderberg electrodes are less expensive than pre-baked electrodes, Söderberg electrodes with larger diameters than pre-baked electrodes can be made and the Söderberg electrode system does not require furnace shutdowns to extend the electrodes (Innvær, 1992; Arnesen et al., 1979).

In Fig. 1 a simplified representation of a typical Söderberg electrode is presented. A Söderberg electrode consists of a cylindrical steel casing extending from a platform located above the furnace down into the furnace (Asphaug and Innvær, 1997; Innvær, 1992; Toromanoff and Habashi, 1989; Arnesen et al., 1979). The electrode casing serves as a mould for the electrode paste that consists of a coal tar pitch binder mixed with a solid filler such as calcined anthracite or coke (Innvær, 1992, 1989, 1983; Toromanoff and Habashi, 1989). Heat from the furnace together with electrical current passing through the casing and casing fins melt the electrode paste (Asphaug and Innvær, 1997; Ord et al., 1995; Innvær, 1992; Innvær et al., 1986; Toromanoff and Habashi, 1989). The solid electrode paste that is added to the top of the electrode casing melts and fills the entire diameter of the electrode casing when it reaches a temperature of approximately 50–100 °C (Wilkinson et al., 2001; Asphaug and Innvær, 1997; Ord et al., 1995; Innvær, 1992; Innvær and Olsen, 1980; Arnesen et al., 1979), depending on the softening temperature of the electrode paste utilised. At a temperature of approximately 400–500 °C the electrode paste is baked into a solid carbonaceous electrode (McDougall et al., 2004; Andersen et al., 2001; Asphaug and Innvær, 1997; Ord et al., 1995; Fitt and Aitchison, 1993; Innvær, 1992; Innvær et al.,

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1986, 1984; Innvær and Olsen, 1980; Arnesen et al., 1979). This temperature is commonly referred to as the baking isotherm temperature. The mechanical strength and electrical conductivity of the electrode increase as the baking process progresses. During the early stages of the electrode baking process, i.e. when the electrode paste is still soft, electrical energy is conducted mainly by the steel electrode casing and the casing fins. At a temperature of 800–1000 °C, the baked carbon electrode is able to conduct the full electrical current (Asphaug and Innvær, 1997; Innvær et al., 1986).

In order to ensure safe, profitable and continues operations many aspects have to be managed in a Söderberg electrode system. These aspects are collectively referred to as electrode management. Notwithstanding the importance of electrode management, relatively little information has been published in the peer reviewed public domain on this topic during the last decade. This sometimes leads to out of date information from literature being utilised in papers. As an example, in a relatively recent paper (Meyjes et al., 2010) a model was introduced to predict some operational aspects of a Söderberg electrode. The thermal expansion data of the electrode paste utilised in this model was based on research published in McDougall et al. (2004), who in turn referred to Innvær et al. (1984) that published the thermal expansion data of a Söderberg electrode paste originating from a single producer. Internationally the raw materials utilised in Söderberg electrode paste production vary significantly, due to the availability of suitable coal tar pitches and solid filler materials. In order to stimulate research focussing on Söderberg electrode management and more specifically electrode paste production, a novel technique utilising thermomechanical analysis (TMA) was developed to determine the thermal dimensional behaviours of Söderberg electrode paste raw materials. In this paper it is demonstrated how this technique can be used to gain insight into important electrode management parameters, and in what manner this technique can be used by Söderberg electrode paste producers to improve the quality of paste produced.

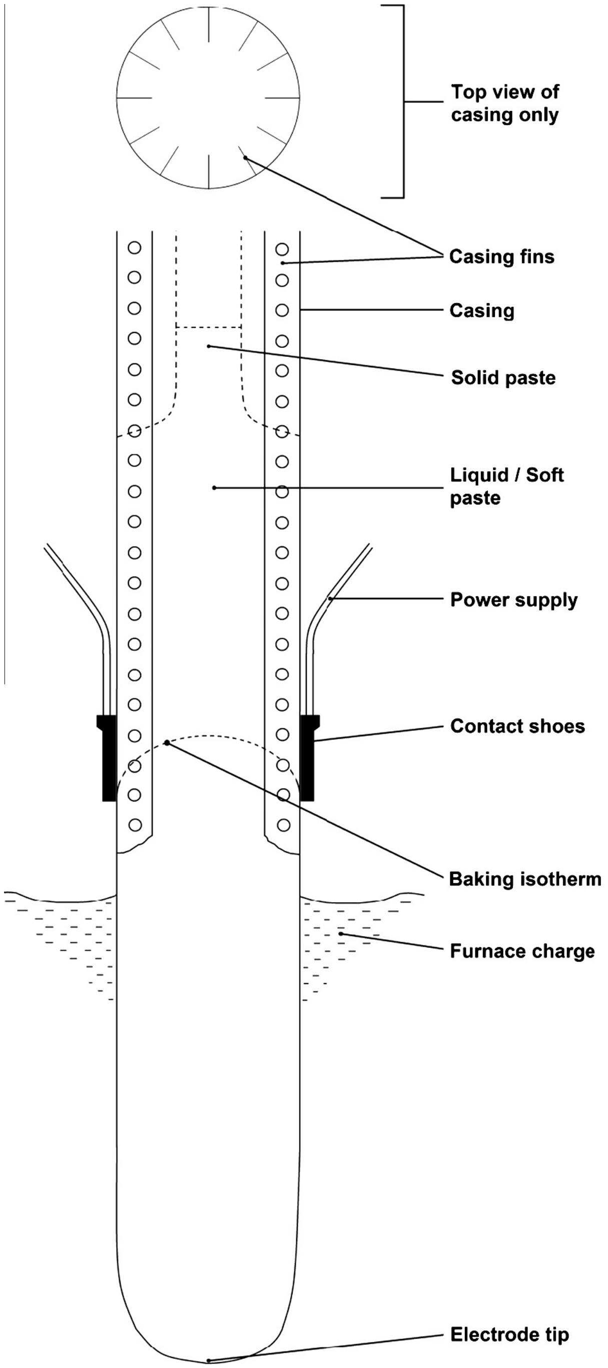

Fig. 1. Simplified representation of a Söderberg electrode, adapted from Arnesen et al. (1979). The main figure at the bottom indicates a side sectional view of the electrode, while the top image indicates the top sectional view of the casing only.

2. Materials and methods

2.1. Materials

As mentioned, Söderberg electrode paste consists of two components, i.e. a binder that is mostly a coal tar pitch and a solid filler, which can be either coke or calcined anthracite (Innvær, 1992, 1989, 1983; Toromanoff and Habashi, 1989). Two coal tar pitch samples were received from the only commercial supplier of coal tar pitch used for the production of Söderberg electrode paste in South Africa. The first sample was a low softening point (LSP) coal tar pitch, while the second sample was a high softening point (HSP) coal tar pitch. Three uncalcined anthracite samples were also obtained from different anthracite mines in South Africa. These specific anthracites are calcined and used in the production of Söderberg electrode paste at one of the largest Söderberg electrode paste producers in South Africa.

Although the focus of this paper was on the raw materials utilised in Söderberg electrode paste production, i.e. coal tar pitch and calcined anthracite, a pre-baked electrode graphite sample was also obtained from the only manufacturer of pre-baked electrodes in South Africa. This facilitated the comparison of measured thermal dimensional behaviours of the Söderberg electrode paste raw materials with a completely baked graphite electrode.

None of the raw material suppliers wanted to be identified. Therefore, the coal tar pitch, anthracite and pre-baked electrode graphite samples were denoted as LSP and HSP coal tar pitch, anthracite A1, A2 and A3, and pre-baked electrode graphite, respectively.

2.2. Methods

2.2.1. Anthracite and coal tar pitch characterisation

In order to characterise the coal tar pitch and anthracite samples received, proximate analyses were conducted with SANS 5925:2007, SANS 131:2011 and SANS 50:2011 methods in order to quantify the moisture, ash and volatile contents, respectively, while the fixed carbon content was determined by difference. Ultimate analyses were also performed to determine the carbon and hydrogen contents with ASTM D5373, the nitrogen content with

ASTM D3179, the sulphur content with ASTM D4239 and the oxygen content by difference.

In addition to the above-mentioned proximate and ultimate analyses, the fundamental properties such as the softening point, coking value, as well as quinoline and toluene insoluble contents of the coal tar pitch samples were determined. The softening points were measured on a Mettler FP 80 HT softening point measurement instrument.

In order to determine the coking value the coal tar pitch samples were crushed to less than 212 μm. 3 ± 0.0005 g of a crushed sample was then weighed and pyrolysed at 900 °C in an inert atmosphere for 30 min in a fit-for-purpose instrumental set-up. The remaining residue was weighed and the percentage coking value calculated.

In the quinoline insoluble analysis, 1 ± 0.0005 g of a crushed (<212 μm) coal tar pitch sample was digested and extracted with 65 ml hot quinoline. Thereafter the residue was filtered off and dried in an oven at 105 ± 5 °C for 60 min. The dried samples were then cooled in a desiccator, weighed and the quinoline insoluble content calculated.

The toluene insoluble content of a coal tar pitch sample was determined by digestion and extraction of 1.5 ± 0.0005 g crushed sample (<212 μm) with 60 ml hot toluene in an alundum thimble for 24 h. The remaining residue was dried at 105 ± 5 °C in an oven for 60 min, after which it was cooled in a desiccator and weighed.

2.2.2. Anthracite calcination

Since calcined anthracite is used as a solid filler in the production of Söderberg electrode paste, the received uncalcined anthracite samples had to be calcined. Boat crucibles (CoorsTek AD-998 99.8% pure aluminium oxide) were filled with 25 g anthracite, which were then heated to maximum temperatures of 1200, 1300 or 1400 °C in an Elite TSH15 tube furnace fitted with a programmable temperature controller. Ceramic heat shields were inserted at both ends of the tube (CoorsTek AD-998 99.8% pure aluminium oxide) to improve the tube length in which a stable working temperature could be achieved. Stainless steel caps that were fitted onto both sides of the ceramic tube to seal the ends were protected from excessive heat by the afore-mentioned ceramic heat shields. The stainless steel caps had a gas inlet on the one side and an outlet on the other. Calcination was conducted under an inert atmosphere of nitrogen (N_2), flowing through the tube furnace at a flow rate of 1.2 NL/min. The furnace was heated for an hour to the required maximum temperature (i.e. 1200, 1300 or 1400 °C) and was held constant at this temperature for another 2 h. Thereafter the furnace was switched off and the samples allowed to cool down inside the furnace, while the N_2 flow was maintained in order to prevent oxidation of the samples.

2.2.3. Sample preparation for TMA

In order to facilitate TMA measurements, cylindrical coal tar pitch and anthracite pellets were produced from the various samples. A procedure similar to procedures described previously (Neizel et al., 2013; Kleynhans et al., 2012; Nel et al., 2011) was used.

Coal tar pitches have relatively low melting points, typically in the range of 50–135 °C, depending on the composition of the coal tar pitch (Shoko et al., 2013). After melting, a coal tar pitch remains a viscous liquid, until carbonisation takes place due to increased temperature. In order to prevent the coal tar pitch samples from softening in the TMA instrument the coal tar pitch samples were thermally pre-treated prior to pelletisation. The lowest thermal pre-treatment temperature that produced a pellet that did not soften in the TMA was determined by heating different coal tar pitch batches of the same sample to maximum temperatures ranging from 400 to 500 °C, in steps of 25 °C, under an inert atmosphere. This was performed in the same equipment and inert gaseous conditions described in Section 2.2.2. After cooling down, the thermally pre-treated coal tar pitches were pulverised using a Siebtechnik pulverizer, until approximately 75% of the particles were smaller than 75 μm. The pulverised coal tar pitch was then pressed into cylindrical pellets in a Specac PT No. 3000 10 mm die set, with an LRX Plus strength testing machine (Ametek Lloyd Instruments) equipped with a 5 kN load cell. For each pellet, 0.8 g pulverised coal tar pitch was placed in the die set and compressed at a rate of 10 mm/min until a load of 2 kN was reached, where after this load was held for 20 s.

Calcined (Section 2.2.2) and uncalcined anthracite samples were pulverised and pelletised in a similar fashion as described above. The only differences in the procedure were that the maximum pressure during pellet pressing was increased to 4.5 kN for 60 s and two droplets of milli-Q water (resistivity 18.2 MΩ cm) were added to the 0.8 g of pulverised material prior to pressing the pellet. This ensured that the anthracite pellets had sufficient strength for handling and subsequent TMA analyses.

Pre-baked electrode graphite pellets of 9 mm in diameter were drilled from rectangular blocks by means of a core drill. The thickness of the rectangular blocks was the same, which ensured each core-drilled pellet had the same height of 10 mm.

Table 1
Proximate and ultimate analyses of the coal tar pitch and anthracite, as well as fundamental properties of the coal tar pitch samples utilised.

	Inherent moisture (%)	Ash content (%)	Volatile matter (%)	Fixed carbon (%)	
Proximate analysis of the coal tar pitch and anthracite on an air dried basis					
LSP coal tar pitch	0.1	0.5	60.7	38.7	
HSP coal tar pitch	0.1	0.5	58.1	41.3	
Anthracite A1	2.2	8.1	4.9	84.8	
Anthracite A2	3.2	18.6	9.5	68.7	
Anthracite A3	1.3	16.2	5.2	77.3	
	Sulphur (%)	Hydrogen (%)	Nitrogen (%)	Carbon (%)	Oxygen (%)
Ultimate analysis of the coal tar pitch and anthracite on a dry ash free basis					
LSP coal tar pitch	0.50	4.2	1.2	91.0	3.1
HSP coal tar pitch	0.53	3.9	1.2	91.1	3.4
Anthracite A1	1.13	2.6	1.9	83.2	1.0
Anthracite A2	0.69	3.1	1.6	71.6	1.2
Anthracite A2	1.20	2.2	1.5	75.0	2.5
	Softening point (°C)	Coking value (%)	Quinoline insoluble (%)	Toluene insoluble (%)	
Fundamental properties of the coal tar pitch samples					
LSP coal tar pitch	65.4	46.6	7.3	22.2	
HSP coal tar pitch	85.0	48.7	7.2	23.2	

2.2.4. TMA measurements

The thermal dimensional behaviour of the thermally pre-treated coal tar pitch, the calcined and uncalcined anthracite and the electrode graphite pellets were monitored with an Exstar SS6300 TMA. A constant N_2 flow rate of 1.2 NL/min was maintained through the TMA instrument to prevent oxidation, which could have an impact on the thermal dimensional behaviours. Each sample was exposed to three consecutive heating and cooling cycles before being removed from the TMA. During the first heating cycle the pellet was heated from room temperature to 1300 °C at a heating rate of 10 °C/min. The sample was then allowed to cool to approximately 100 °C, which was facilitated by the continuous N_2 flow. Thereafter the next heating cycle commenced, utilising the same experimental conditions.

2.2.5. Statistical handling of the TMA data

Each TMA result presented was calculated from the average of three separate TMA analysis of a specific material. All data processing and figures compiled from this data were conducted with a fit-for-purpose Matlab (Mathworks, 2013) program set.

3. Results and discussion

3.1. Raw material characterisation

The proximate and ultimate analyses of the coal tar pitch and anthracite samples, as well as the fundamental properties (i.e. softening point, coking value, quinoline insoluble content and toluene insoluble content) of the coal tar pitch samples utilised as case study materials in this paper are presented in Table 1. These material properties are indicative of the raw materials currently being utilised during the production of Söderberg electrode paste in South Africa. However, the properties of materials utilised in Söderberg electrode paste production can differ from the case study materials utilised. As an example, Shoko et al. (2013) evaluated 12 different coal tar pitches, utilised in Söderberg electrode paste production internationally. These authors (Shoko et al., 2013) reported softening points in the range 65–135 °C, while the case study LSP and HSP coal tar pitches had softening points of 65.4 and 85 °C, respectively. The case study materials utilised in this study should therefore be considered as typical, but do not represent all possible compositions.

3.2. TMA analysis

3.2.1. Softening behaviour of thermally pre-treated coal tar pitch

The dimensional behaviour of the LSP coal tar pitch sample thermally pre-treated at different maximum temperatures is presented in Fig. 2. Although the dimensional behaviour results of the HSP coal tar pitch sample are not shown, it behaved similarly. Pellets prepared from coal tar pitch thermally pre-treated at 400 °C indicated sudden shrinkage if heated above 400 °C, which coincided with melting of the coal tar pitch. Pellets prepared from coal tar pitch thermally pre-treated at 450 °C expanded rapidly at temperatures exceeding the pre-treatment temperature. Although an expansion was observed, this expansion correlated to melting of the core of the pellet that subsequently sagged out at the bottom of the pellet. The TMA probe only maintains a very small force on a sample pellet being measured. The liquid sagging out at the bottom of the pellet raised the entire pellet, which was therefore recorded as an expansion. In contrast, coal tar pitch pellets prepared from samples thermally pre-treated at 475 and 500 °C indicated gradual dimensional changes, indicating that no melting occurred.

The above-mentioned minimum pre-treatment temperature, which did not result in subsequent melting of the thermally

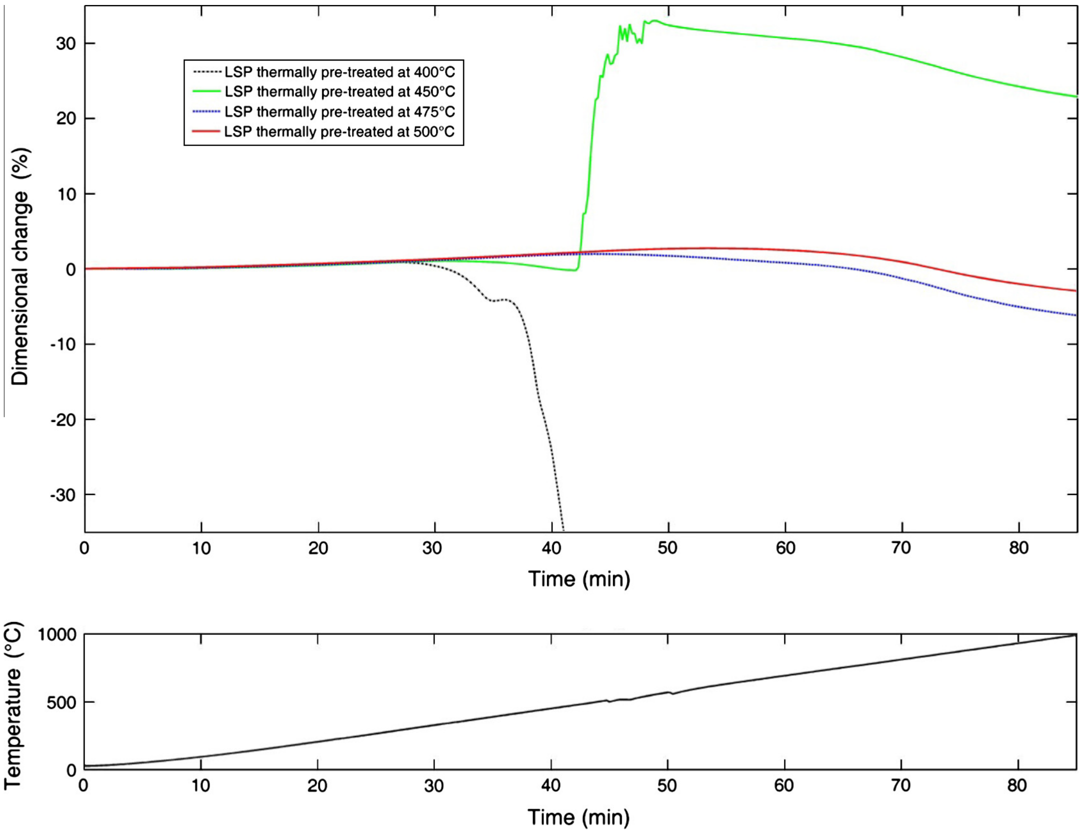

Fig. 2. The dimensional behaviour of LSP coal tar pitch pellets thermally pre-treated at 400, 450, 475 and 500 °C, respectively. TMA measurements were conducted at a constant heating rate of 10 °C/min. The temperature profile is indicated by the secondary figure, below the main figure.

pre-treated coal tar pitch in the TMA is of great industrial significance. The baking isotherm temperature (Fig. 1) is an important parameter during Söderberg electrode management. This temperature indicates the minimum temperature that must be achieved during the *in situ* baking process before a Söderberg electrode can support itself. At this temperature the coal tar pitch serving as binder in the electrode paste has transformed from a liquid to a solid carbonaceous material. Current literature indicates the baking isotherm temperature to be in the range of 400–500 °C (McDougall et al., 2004; Andersen et al., 2001; Asphaug and Innvær, 1997; Ord et al., 1995; Fitt and Aitchison, 1993; Innvær, 1992; Innvær et al., 1986, 1984; Innvær and Olsen, 1980; Arnesen et al., 1979). However, more accurate determination of the baking isotherm temperature of a particular coal tar pitch binder of the electrode paste at a specific smelting operation will substantially enhance electrode management at that facility. It is acknowledged that the melting behaviour of electrode paste, which is a mixture of the coal tar pitch binder and solid filler (e.g. calcined anthracite or coke) may differ from the behaviour of the coal tar pitch alone. However, the melting behaviour of electrode paste will mainly depend on the binder and not on the solid filler. The temperature at which the coal tar pitch binder transforms from a liquid to a solid carbonaceous material should therefore be a good approximation of the baking isotherm temperature of a Söderberg electrode produced from an electrode paste containing that particular coal tar pitch binder. The baking isotherm temperature was established to be between 450 and 475 °C for the two case study coal tar pitch samples utilised in this study, since the coal tar pitch samples melted in the TMA if thermal pre-treatment was below 450 °C, while samples did not melt if the pre-treatment temperature was 475 °C. These results do not imply that all coal tar pitches utilised in Söderberg electrode paste production would have a baking isotherm temperature in this temperature range. It does, however, indicate that the measurement technique developed can be used to determine this important transitional temperature more accurately than previously possible. This newly developed method is currently being applied by Shoko et al. (2013), who have investigated the differences in the baking isotherm temperature of twelve coal tar pitch samples obtained from most of the internationally well-known Söderberg electrode paste producers.

3.2.2. TMA of coal tar pitch thermally pre-treated above the baking isotherm temperature

Since it was established in the previous section (Section 3.2.1) that the case study coal tar pitch samples had to be thermally pre-treated at 475 °C to avoid the pellets from melting in the TMA, all subsequent coal tar pitch pellets were prepared from coal tar pitch thermally pre-treated at 475 °C in an inert atmosphere (Section 2.2.3). The dimensional behaviours (TMA measurements) of the LSP and HSP coal tar pitch pellets prepared from thermally pre-treated samples are presented in Fig. 3.

As is evident from the results, both the LSP and HSP coal tar pitches thermally pre-treated at 475 °C behaved similar during all three thermal cycles. However, the dimensional behaviours of both the pitches were significantly different in the first thermal cycle (0 to ~250 min), than in the second and third thermal cycles (250 min onwards), which were similar.

During the first thermal cycle, a small expansion occurred when the pellet was heated from room temperature to approximately 475 °C. This initial expansion was caused by the thermal expansion

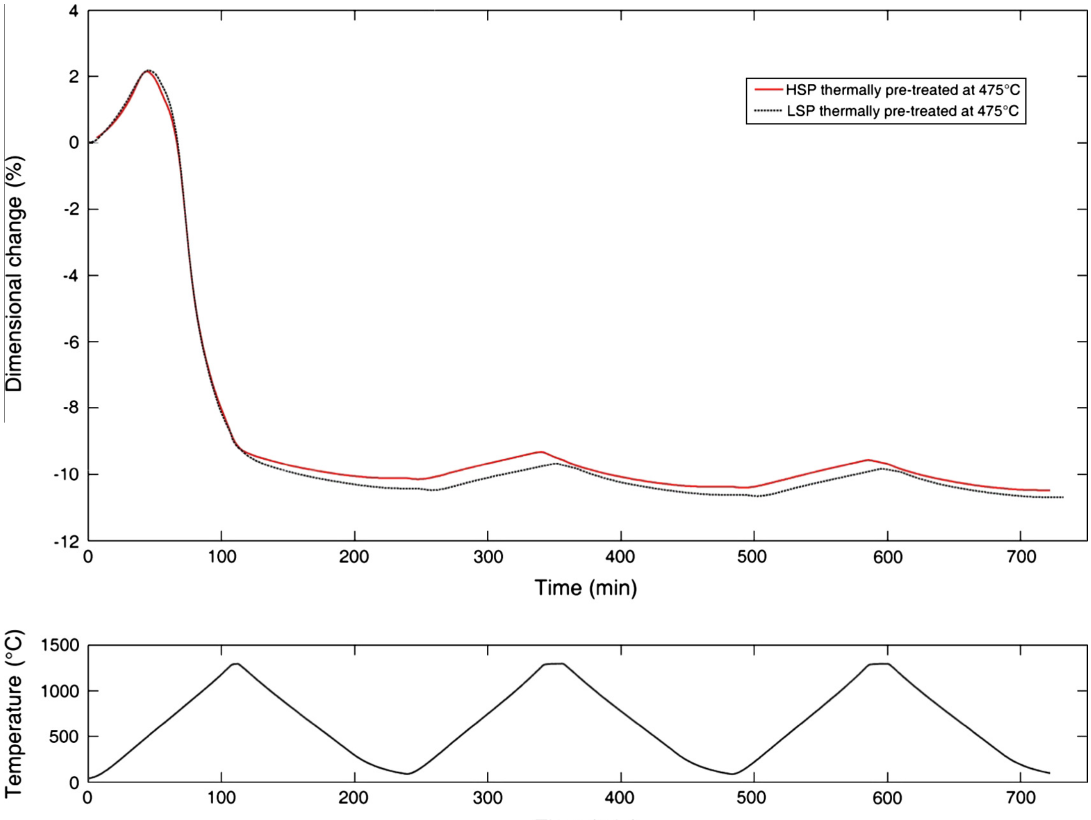

Fig. 3. The thermal dimensional behaviour of LSP and HSP coal tar pitch samples thermally pre-treated at 475 °C. The temperature was cycled three times from room temperature to 1300 °C in the TMA, utilising a constant heating rate of 10 °C/min. These thermal cycles are indicated by the secondary figure, below the main figure.

of the coal tar pitch pellet that acted similarly to a solid material thermally expanding, since the coal tar pitches were already thermally pre-treated up to 475 °C prior to the TMA analysis. However, the dimensional behavioural data during the first heating cycle up to this temperature (475 °C) gives little insight into the fundamental properties of the material, since thermal dimensional changes of the pitches could not be measured in the temperature range where the coal tar pitches were soft (⩽475 °C). In the previous section (Section 3.2.1) the lowest pre-treatment temperature where softening and melting of the coal tar pitches did not occur, i.e. correlating to the baking isotherm temperature, was determined. However, no detailed dimensional data was obtained below 475 °C. At temperatures above 475 °C the pre-treated coal tar pitch pellets shrunk, which continued up to the maximum temperature investigated (1300 °C). For both the case study coal tar pitches the total shrinkages were approximately 12% during the first thermal cycle, after the initial thermal expansion of the pellets.

In contrast to the first thermal cycle the amplitudes of thermal expansion and contraction during the second and third TMA thermal cycles were relatively small, i.e. approximately 2%.

The difference in the magnitude of the dimensional changes between the first and subsequent thermal cycles can be attributed to structural reordering of the carbonaceous material that took place during the first thermal cycle in the TMA. During the first thermal cycle the coal tar pitches were heated up to 1300 °C for the first time. During the second and third TMA thermal cycles, the coal tar pitches had already been exposed to a maximum temperature of 1300 °C, hence little additional structural reordering took place.

Application of the above-mentioned method to quantify the dimensional behaviour of coal tar pitch binders utilised in Söderberg electrode paste production could provide valuable information with regard to electrode management. In particular for the area just below the contact shoes (Fig. 1), i.e. from the baking isotherm further down into the furnace zone. The large shrinkage (approximately 12% for both the LSP and HSP tar pitch binders), which occurred during the first heating cycle, indicates that the electrode is most vulnerable to failure during the initial baking process. During this baking process the electrode becomes increasingly stable with regard to thermal dimensional changes, as structural reordering of the carbonaceous binder takes place. This was confirmed by the second and third thermal cycles of the LSP and HSP tar pitches, during which the dimensional changes that occurred were approximately 2%. To put these results into perspective, it can be stated that the dimensional changes of the case study coal tar pitch binders during the first TMA thermal cycle were approximately six fold more than the dimensional changes that occurred in subsequent thermal cycles. It cannot be stated with certainty that all coal tar pitch binders used for Söderberg electrode paste production will react similarly than the case study materials utilised in this study. However, the results clearly indicate how TMA can be used to quantify the dimensional behaviour of a specific coal tar pitch binder utilised in Söderberg electrode paste production.

3.2.3. TMA of calcined anthracite

Since calcined anthracite is used as a filler in the production of Söderberg electrode paste (Innvær, 1992, 1989, 1983; Toromanoff and Habashi, 1989), the thermal dimensional behaviours of calcined anthracites were also considered. The behaviour of uncalcined anthracites will be discussed in the next section (Section 3.2.4).

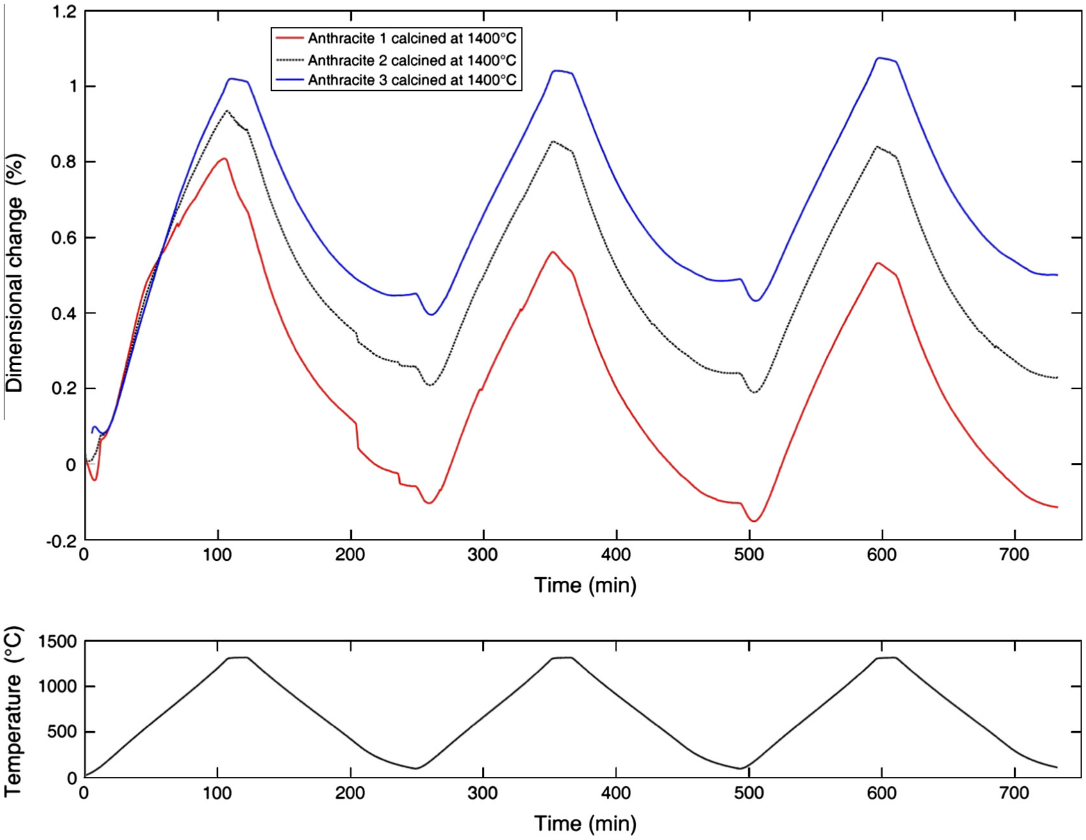

Fig. 4. The thermal dimensional behaviour of pellets prepared from the three case study anthracites samples calcined at 1400 °C. The temperature was cycled three times from room temperature to 1300 °C in the TMA, utilising a constant heating rate of 10 °C/min. These thermal cycles are indicated by the secondary figure, below the main figure.

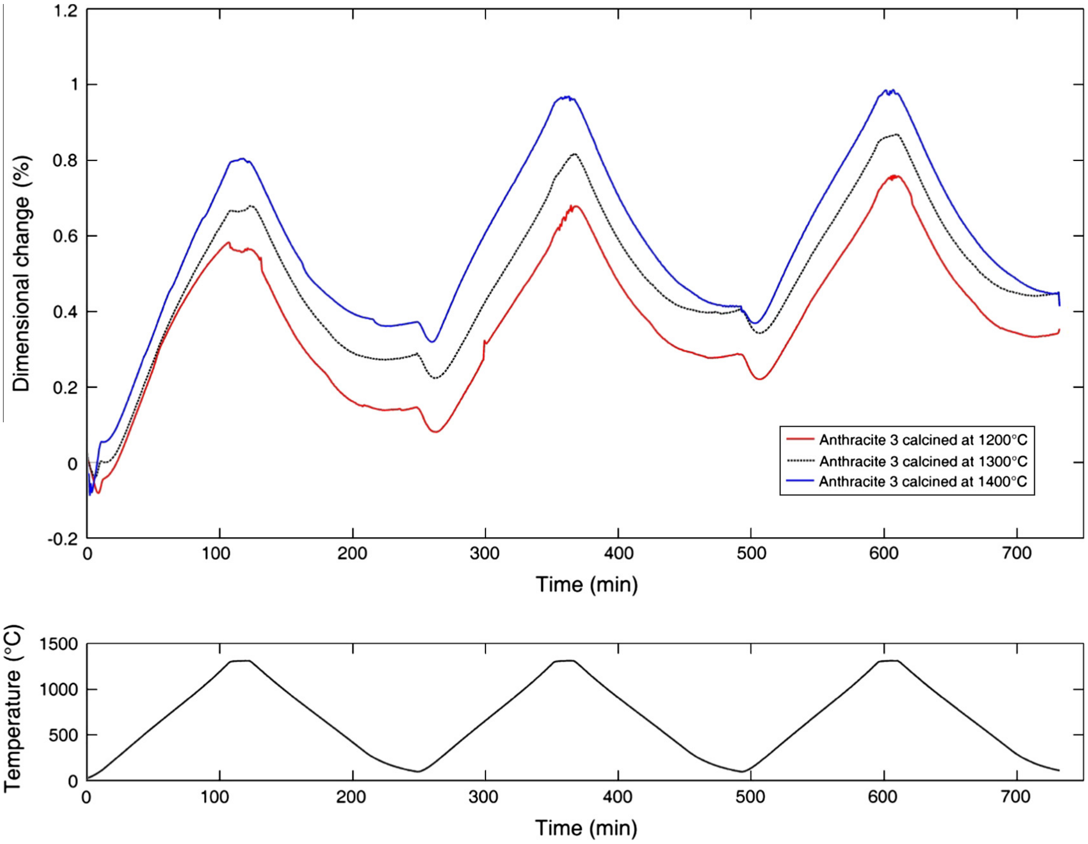

Fig. 5. The thermal dimensional behaviour of pellets prepared from anthracite 3, calcined at 1200, 1300 and 1400 °C, respectively. The temperature was cycled three times from room temperature to 1300 °C in the TMA, utilising a constant heating rate of 10 °C/min. These thermal cycles are indicated by the secondary figure, below the main figure.

The dimensional behaviours of pellets made from the three case study anthracites calcined at 1400 °C are presented in Fig. 4. It is evident that the amplitudes of dimensional changes for all three calcined anthracites were in the order of 0.6–1.0%. Also, the thermal dimensional behaviour did not change significantly between the three TMA thermal cycles. The relatively small dimensional changes and relatively consistent behaviours during all three thermal cycles were expected, since the anthracite pellets were prepared from anthracites calcined (Section 2.2.2) at 1400 °C. Due to this prior thermal treatment (calcination at 1400 °C) no significant additional structural reordering had taken place during these TMA thermal cycles.

The influence of calcination temperature on the thermal dimensional behaviours of the pellets made from the case study calcined anthracites are illustrated in Fig. 5, which presents data for anthracite 3 as an example. It is evident from the first TMA thermal cycle (0–250 min) that higher calcination temperatures resulted in smaller dimensional changes.

All the above-mentioned results related to the thermal dimensional behaviour of calcined anthracites have significant industrial relevance and demonstrate the usefulness of the methods discussed in this paper. During the initial baking of a Söderberg electrode, the conductivity of the electrode is largely dependent on the steel casing and fins (Fig. 1), since the unbaked electrode paste is not very conductive. The calcined anthracite filler that is part of the electrode paste is calcined prior to paste production in order to improve the initial conductivity of the Söderberg electrode paste. The conductivity of carbon increases as the structure approaches the structure of graphite (Asphaug and Innvær, 1997). Other reasons for calcining the anthracite prior to electrode paste production are to drive off the volatile organic compounds and to stabilise the anthracite dimensionally (Asphaug and Innvær, 1997; Stanko, 1972). Results obtained for all three case study calcined anthracite samples indicated thermal dimensional changes of less than 1%. The anthracite samples calcined at the higher experimental calcination temperatures (1400 °C) prior to TMA analysis, had the smallest dimensional changes. This proved that higher calcination temperatures indeed result in a higher level of structural ordering and dimensional stability. The efficiency of the calcination process of the anthracite prior to Söderberg electrode paste production is therefore extremely important in order to produce dimensionally stable electrodes. The method discussed in this paper can be used by producers of Söderberg electrode pastes to ensure the efficiency of their calcination processes to yield the required quality calcined anthracite. Additionally, if the calcined anthracite thermal dimensional results are considered in context of the results obtained for the coal tar pitches thermally pre-treated at 475 °C (Section 3.2.2), the importance of the initial baking of a Söderberg electrode at temperatures exceeding the baking isotherm temperature is again stressed. During this initial electrode baking process, the dimensional behaviours of the tar pitch binder and the calcined anthracite differ dramatically – the tar pitch binder undergoes shrinkage of approximately 12%, while the calcined anthracite expands up to 1%. This difference in magnitude of thermal dimensional behaviour (12% *vs.* ⩽1%) and difference in motion (shrinkage *vs.* expansion) can result in thermal stress building up in the electrode.

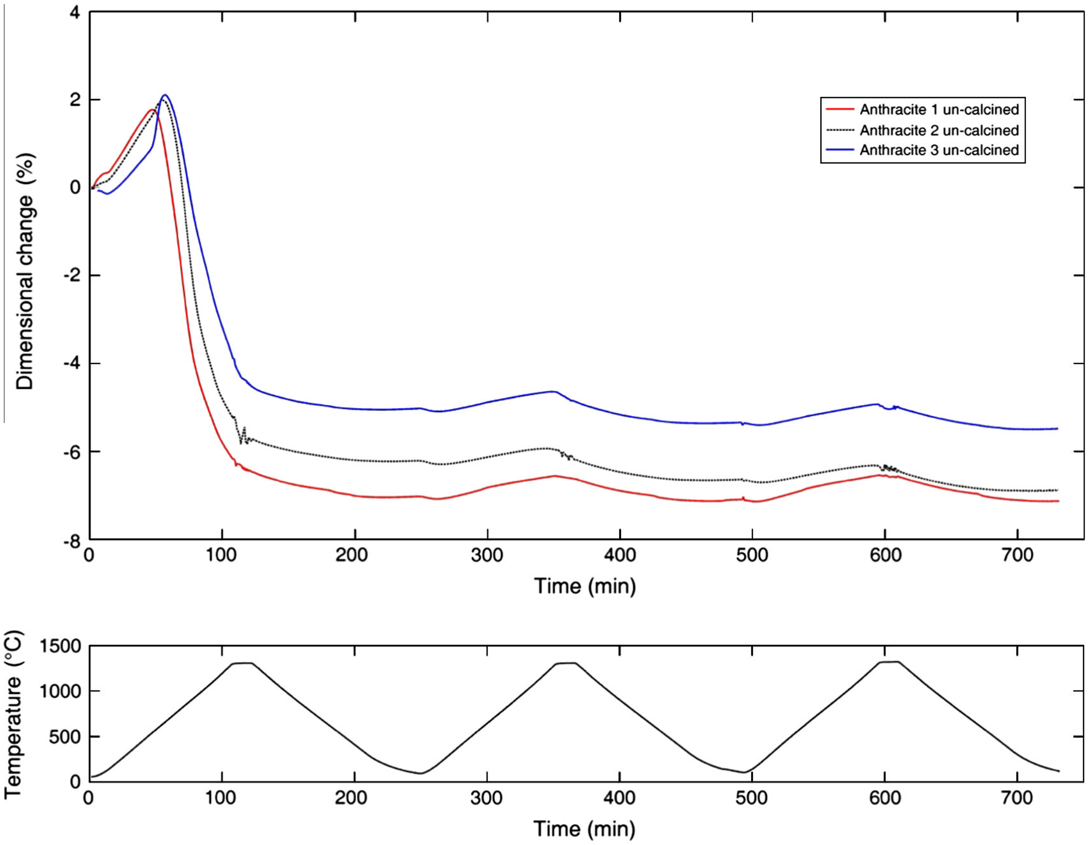

Fig. 6. The thermal dimensional behaviour of pellets prepared from the three case study uncalcined anthracites. The temperature was cycled three times from room temperature to 1300 °C in the TMA, utilising a constant heating rate of 10 °C/min. These thermal cycles are indicated by the secondary figure, below the main figure.

3.2.4. TMA of uncalcined anthracite

The dimensional behaviours measured with TMA of pellets prepared from the three case study uncalcined anthracite samples are presented in Fig. 6.

In contrast to the relatively small thermal dimensional changes observed for the calcined anthracite samples (Section 3.2.3), the dimensional changes of the uncalcined samples during the first TMA thermal cycle were significantly larger, which ranged from 6–8%. Again, these results stress the importance of the efficiency of the calcination process of the anthracite prior to Söderberg electrode paste production as explained in Section 3.2.3. Incomplete calcination of anthracite prior to introducing it as the solid filler in Söderberg electrode paste will result in additional thermal dimensional changes occurring during the initial baking of the Söderberg electrode, resulting in added thermal stress build-up in the electrode.

3.2.5. TMA of pre-baked electrode graphite

The main objective of this paper was to demonstrate the efficiency of using TMA to characterise the thermal dimensional behaviours of Söderberg electrode paste raw materials. Electrode graphite is not a Söderberg electrode paste raw material, but can rather be considered as the end product of the thermal reordering process during the *in situ* baking of a Söderberg electrode in a SAF. Characterisation of the thermal dimensional behaviour of typical electrode graphite will therefore contextualise the thermal dimensional results of the electrode past raw materials presented in this paper.

The thermal dimensional behaviours of pellets produced from the pre-baked electrode graphite are demonstrated in Fig. 7. Since these samples were taken from actual electrode graphite that was pre-baked at temperatures in the order of 3000 °C (temperature provided by pre-baked electrode producer), it can be stated with confidence that the carbon structure of these samples had been converted to maximum structural ordering, i.e. graphite. It was therefore not surprising that the dimensional changes of the electrode graphite samples were relatively small (~0.5%). In addition, no significant differences were observed between the three TMA thermal cycles.

Considering all the results presented in this paper in context of the electrode graphite results, it is evident that although the completely baked Söderberg graphite electrode exhibit relatively small thermal dimensional changes (~0.5%), the thermal dimensional changes of the Söderberg electrode paste raw materials are much more significant, i.e. up to 1% for the calcined anthracite and approximately 12% for the coal tar pitch binder. Combined these results indicate that a completely baked Söderberg electrode, i.e. graphite, will be very resilient to electrode breaks due to thermal shock (e.g. furnace downtime and subsequent start-up). However, Söderberg electrodes baked up to the phase where the differences in thermal dimensional behaviours of the coal tar pitch binder and the calcined anthracite filler of the paste impart thermal stress in the electrode will be much more susceptible to electrode breaks. This is especially true for the area of the electrode just below the baking isotherm temperature (Fig. 1). Although these risks are relatively well known within the SAF smelting industry, according to the authors this is the first time that a relatively comprehensive study of thermal dimensional behaviours of the Söderberg electrode paste raw materials has been quantified and the risk scientifically described.

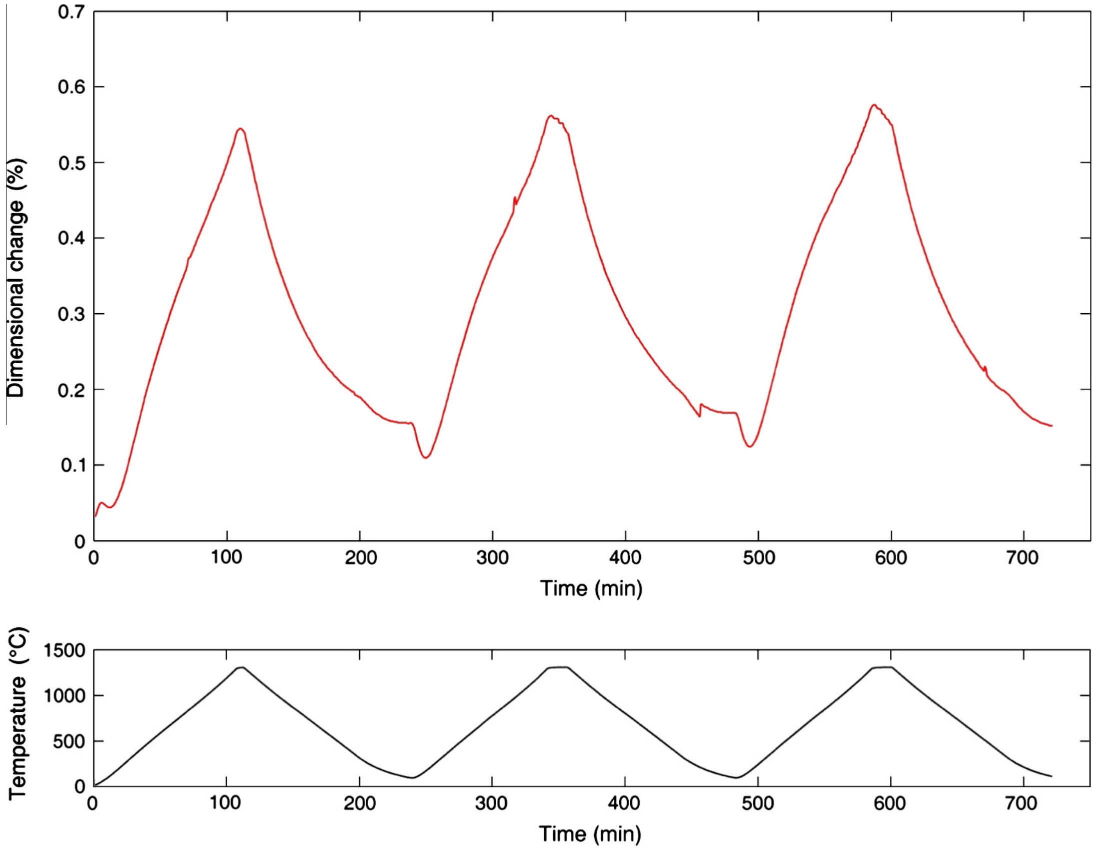

Fig. 7. The thermal dimensional behaviour of typical pre-baked electrode graphite. The temperature was cycled three times from room temperature to 1300 °C in the TMA, utilising a constant heating rate of 10 °C/min. These thermal cycles are indicated by the secondary figure, below the main figure.

4. Conclusions

The TMA method to determine the baking isotherm temperature of a coal tar pitch described in this paper can be used to determine this important temperature more accurately than before. Better knowledge of the baking isotherm temperature will be beneficial for all aspects of electrode management at smelters using a specific electrode paste for which the coal tar pitch binder was characterised.

Other results clearly indicated the conflicting nature in the dimensional behaviour of the case study coal tar pitch binders that shrunk approximately 12% during the first thermal cycle at temperatures above the baking isotherm temperature and the case study anthracites calcined at 1400 °C that expanded 0.6–1.0%. This indicates the vulnerability of a Söderberg electrode baked for the first time at temperatures exceeding the baking isotherm temperature. Additionally the importance of the efficiency of the calcination process of the anthracite prior to Söderberg electrode paste production was demonstrated by TMA measurements that indicated that the case study uncalcined anthracites shrunk 6–8% during the first thermal exposure cycle. These results indicated that the developed TMA method can be used by Söderberg electrode paste producers to do quality control on calcined anthracite, before it is introduced into the Söderberg electrode paste. The method can also be used to evaluate and compare Söderberg electrode paste raw materials, which will enable producers to choose raw materials that will be most compatible in terms of thermal dimensional behaviours.

Comparison of the Söderberg electrode paste thermal dimensional results with that of pre-baked electrode graphite gave a scientific explanation why a partially baked Söderberg electrode (not yet graphite) is so susceptible to breakage caused by thermal shocks.

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References

Andersen, G., Innvær, R., Larsen, B., 2001. Operation of Söderberg electrodes. Methods to avoid and solve electrode failures. In: Proc. of INFACON IX. Qubec City, Canada. pp. 494–500.

Arnesen, A.G., Økstad, S., Innvær, R., Olsen, L., 1979. Operation of Söderberg electrodes. Proc. of the Elkem seminar on smelting. Rio de Janeiro, Brasil.

Asphaug, B, Innvær, R., 1997. Introduction to the Söderberg electrode. Boxer Technologies AS for Elkem Carbon, Kristiansand, Norway.

Fitt, A.D., Aitchison, J.M., 1993. Determining the effective viscosity of a carbon paste used for continuous electrode smelting. Fluid Dynamics Research 11, 37–59.

Innvær, R., 1983. The Söderberg electrode system. Metal Bulletin Monthly 155, 25–27.

Innvær, R., 1989. The Söderberg electrode system, recent research and development, new challenges. In: Proc. of INFACON V. New Orleans, USA. pp. 216–226.

Innvær, R., 1992. A status for the Söderberg smelting electrode. In: Proc. of UIE, Electrotech 92. Montreal, Canada.

Innvær, R., Olsen, L., 1980. Calculation of the thermal stresses in Söderberg electrodes. In: Proc. of UIE9. Cannes, France.

Innvær, R., Olsen, L., Vatland, A., 1984. Operational parameters for Söderberg electrodes from calculations, measurements and plant experience. In: Proc. of Mintek 50. Johannesburg, South Africa. pp. 787–794.

Innvær, R., Fidje, K., Ugland, R., 1986. Effect of current variations on material properties and thermal stresses in Söderberg electrodes. Proc. of INFACON IV. Rio de Janeiro, Brasil, pp. 321–330.

Kleynhans, E.L.J., Beukes, J.P., Van Zyl, P.G., Kestens, P.H.I., Langa, J.M., 2012. Unique challenges of clay binders in a pelletised chromite pre-reduction process. Minerals Engineering 34, 55–62.

Mathworks, 2013. <http://www.mathworks.com/products/matlab/> (accessed 22.01.13).

McDougall, I., Smith, C.F.R., Olmstead, B., Gericke, W.A., 2004. A finite element model of a Söderberg electrode with an application on casing design. In: Proc. of INFACON X. Cape Town, South Africa. pp. 575–583.

Meyjes, R.P., Venter, J., Van Rooyen, U., 2010. Advanced modelling and baking of electrodes. In: Proc. of INFACON XII. Helsinki, Finland. pp. 779–788.

Neizel, B.W., Beukes, J.P., Van Zyl, P.G., Dawson, N.F., 2013. Why is $CaCO_3$ not used as an additive in the pelletised chromite pre-reduction process? Minerals Engineering 45, 115–120.

Nel, M.V., Strydom, C.A., Schobert, H.H., Beukes, J.P., Bunt, J.R., 2011. Comparison of sintering and compressive strength tendencies of a model coal mineral mixture heat-treated in inert and oxidizing atmospheres. Fuel Processing Technology 92 (5), 1042–1051.

Ord, R.J., Schofield, J.G., Tan, C.G., 1995. Improved performance of Söderberg electrodes. CIM Bulletin 88, 97–101.

Shoko, L., Beukes, J.P., Strydom, C.A., 2013. Determining the baking isotherm temperature of Söderberg electrodes and associated structural changes. Accepted for publication in Minerals Engineering.

Stanko, J.S., 1972 and re-issued 1975. The breakage of Söderberg electrodes. National Institute for Metallurgy, Report number 1489. Johannesburg, South Africa.

Toromanoff, I., Habashi, F., 1989. Historical metallurgical notes. Carl Wilhelm Söderberg (1876–1955). CIM Bulletin 82, 90–92.

Wilkinson, P.M., Ganguly, S., William, P.A., Jensen, L.J., 2001. Impact of electrodes paste on Söderberg electrode performance. In: Proc. of INFACON IX. Qubec City, Canada. pp. 510–521.

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Determining the baking isotherm temperature of Söderberg electrodes and associated structural changes ☆

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ABSTRACT

One of the most commonly employed electrode systems in industrial metal smelting applications is continuous self-baking electrodes, i.e. the Söderberg electrode system. In this system, the temperature at which transition from a liquid/soft paste to a solid carbonaceous electrode takes place is termed the baking isotherm temperature. This temperature is extremely important within the context of electrode management. In this paper, thermo mechanical analysis (TMA) was used to measure the dimensional changes that take place in coal tar pitch in the temperature range relevant to the determination of the baking isotherm temperature. It was found that the baking isotherm temperature of coal tar pitches was between 450 and 475 °C, irrespective of the initial chemical composition and physical characteristics of the coal tar pitch. Subsequent Fourier Transform Infra-Red (FTIR) analyses indicated that all coal tar pitches underwent similar compositional changes during the transition from a molten/liquid coal tar pitch to a solid carbonaceous material.

1. Introduction

In the operation of submerged arc furnaces, electrodes conduct electrical energy from a transformer(s) to the smelting zone inside the furnace. For the past century one of the most commonly employed electrode systems in industrial metal smelting applications has been continuous self-baking electrodes, i.e. the Söderberg electrode system (Innvaer et al., 1984). Fig. 1 shows a diagrammatical presentation of the cross-sectional view of a typical Söderberg electrode column.

In the Söderberg electrode system the continuous arcing of the electrode tips results in the consumption thereof. In order to enable the growth of the electrodes *in situ*, solid electrode paste cylinders or blocks are loaded into the metal electrode casings (Nelson and Prins, 2004). Electrode paste is a mixture of coal tar pitch (binder) and filler (e.g. coke or calcined anthracite) (Sem, 1954; Mason, 1970; Innvaer, 1989; Nelson and Prins, 2004). As the paste moves downward in the electrode column, it is heated by the electrical current passing through the contact shoes into the metal electrode casing, as well as heat conducted up the electrode column from the furnace. When the electrode paste is heated to above its softening temperature, it fills the entire electrode column with liquid/soft electrode paste (Fitt and Aitchison, 1993). Continued baking, via the two afore-mentioned mechanisms results in the formation of a solid carbonaceous electrode. The temperature at which transition from a liquid/soft paste to a solid carbonaceous electrode takes place is termed the baking isotherm temperature (Innvaer et al., 1984).

The Söderberg electrode baking isotherm is an extremely important temperature in electrode management. If the electrode is grown (extended) so that the baking isotherm is below the contact shoes, it could have disastrous consequences. The electrode is extremely vulnerable to breakage if the baking isotherm is below the contact shoes, since the liquid/soft electrode paste does not contribute to the mechanical strength of the electrode column. Furthermore, if a hole is arced into the metal casing, liquid/soft paste could run into the furnace. This is usually termed a green electrode break. A green electrode break could result in an explosion, due to the liquid/soft electrode paste being exposed to the very high temperatures inside the furnace. It is therefore vital for continuous, safe and profitable operation that the Söderberg electrode baking isotherm is kept above the contact shoe level under normal furnace operational conditions. Under circumstances when the electrode is grown beyond the Söderberg electrode baking isotherm, special precautions need to be taken, e.g. cutting back on the current being passed through the electrode to avoid arcing holes into the metal casing and not tapping/draining the furnace to limit mechanical forces acting on the electrode column.

According to literature, the baking isotherm of Söderberg electrodes lies in the temperature range of between 400 and 500 °C

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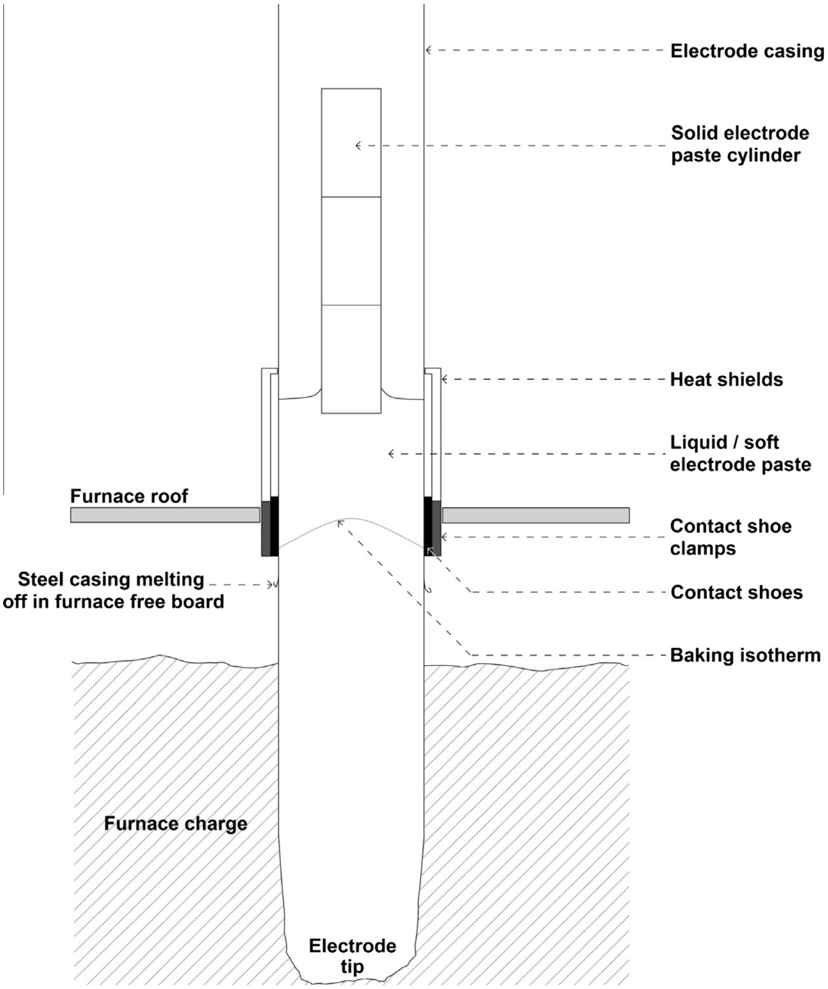

Fig. 1. A diagrammatical presentation of a cross section of a typical Söderberg electrode column.

(Innvaer and Olsen, 1980; Walker, 1986; McDougall et al., 2004; Meyjes et al., 2010). Considering the importance of this isotherm temperature, there is a need to determine this temperature more accurately. It was recently indicated how thermomechanical analysis (TMA) could be used to determine the characteristics of Söderberg electrode paste raw materials, as well as electrode graphite (Beukes et al., 2013; Roos, 2011). In this paper, the TMA method developed by Beukes et al. (2013) is used to determine the Söderberg electrode baking isotherm temperature of 12 coal tar pitch (CTP) samples with a wide spread of chemical compositions and properties. Fourier Transform Infra-Red (FTIR) spectroscopy analysis was also used to determine how the composition of the organic compounds (in term of the functional groups) present in the CTP changed during the transition from the liquid to the solid paste at the baking isotherm temperature.

2. Materials and methods

2.1. Materials

Twelve CTP samples were obtained from various producers throughout the world that supply CTPs to Söderberg electrode paste producers. Most of these CTP suppliers requested to remain anonymous; therefore the CTP samples were denoted as CTP 1 to CTP 12 only.

2.2. Methods

2.2.1. Coal tar pitch characterization

In order to characterise the CTP samples, the proximate and ultimate analyses were determined, in addition to fundamental properties such as the softening point (SP), coking value (CV), as well as quinoline insoluble (QI) and toluene insoluble (TI) contents. These CTP characteristics are the most widely considered properties in the CTP processing industry (Monge et al., 2001).

During the ultimate analyses, the carbon and hydrogen contents were determined using a method based on ASTM D5373, nitrogen based on ASTM D3179, sulphur based on ASTM D4239 and oxygen by difference. For proximate analysis, the moisture was analysed with SANS 5925, volatiles with ISO 562, and ash and fixed carbon were determined using ISO 1171.

The SPs of the CTP samples were measured on a Mettler FP 80 HT softening point measurement instrument. The SP measurements were recorded to the nearest 0.1 °C and performed in duplicate. The reported results were calculated as the average of the two separate readings.

For the CV determinations, CTP samples were crushed to a particle size smaller than 212 µm. 3 ± 0.0005 g of this crushed sample was weighed and pyrolysed at 900 °C in an inert environment for 30 min in a fit-for-purpose instrumental set-up for determining CV at the quality control laboratory of a South African graphite electrode producer. The remaining residue was weighed and the percentage CV calculated.

In the QI analysis, 1 ± 0.0005 g of a crushed CTP sample was digested and extracted with 65 ml hot quinoline. Thereafter, the residue was filtered off and dried in an oven at 105 ± 5 °C for 60 min, after which the dried samples were cooled in a desiccator and weighed. The QI contents were expressed as percentages.

The TI content of a CTP sample was determined through the digestion and extraction of 1.5 ± 0.0005 g crushed sample with 60 ml hot toluene in an alundum thimble for 24 h. The remaining residue was dried at 105 ± 5 °C in an oven for 60 min, after which it was cooled in a desiccator and weighed.

2.2.2. Sample preparation prior to TMA analysis

As-received CTP samples could not be analysed in the TMA instrument utilised in this study, as the TMA probe resting on top of the CTP sample in the TMA instrument protruded into the CTP if the sample was heated above the SP of the specific CTP (Beukes et al., 2013). It was therefore required to thermally pre-treat the CTP samples to ensure that the sample would not soften inside the TMA during an analysis.

During thermal pre-treatment a Coorstek ceramic crucible (99.8% pure aluminium oxide) was filled with 25 g of CTP sample. The crucible with the sample was then placed in an Elite THS 15 tube furnace equipped with a programmable temperature control. Ceramic heat shields were inserted at both ends of the tube furnace to minimise heat loss and to improve the tube length in which a stable working temperature could be achieved. These heat shields also protected the stainless steel caps, which were fitted onto both sides of the ceramic tube to seal the ends. The stainless steel caps had a gas inlet on the one side and an outlet on the other. During all CTP thermal pre-treatments an inert gaseous atmosphere was maintained by a constant flow of 1 NL/min of N_2 through the furnace. Before any CTP pre-treatment experiment commenced, the furnace loaded with the CTP sample was flushed with N_2 at a flow rate of 1 NL/min for 3 min. This ensured that no oxidation of the CTP sample occurred during the thermal pre-treatment. The furnace was programmed to ramp up from room temperature to the desired maximum temperature in 60 min; where after a holding time of 120 min was maintained. The furnace was then switched off and the heated CTP sample allowed to cool down in the furnace, under the inert atmosphere. Thereafter, the thermally pre-treated CTP sample was removed from the furnace and stored in a sealed container.

After the above-mentioned thermal pre-treatment, the CTP samples had to be reshaped into a form that could be utilised in subsequent TMA analyses. For this purpose, the thermal pre-treated CTP samples were pulverised and pressed into cylindrical pellets, similar to the procedures described previously (Neizel et al., 2013; Kleynhans et al., 2012; Nel et al., 2011). The pulverisation was performed on a Sibetechnik laboratory disc mill with a tungsten carbide grinding chamber. Approximately 20 g of pre-treated sample was pulverised for 30 s. 0.65 ± 0.1 g of pulverised pre-treated CTP sample was then weighed and transferred into a Specac PT No. 3000 cylindrical 10 mm diameter die set. The powdered CTP pre-treated sample was then compressed into a pellet with an LRX Plus material strength testing machine (Ametek Lloyd Instruments) fitted with a 5 kN load cell. The compression arm was lowered at a speed of 10 mm/min until a load of 3.5 kN was reached, where after it was held for 30 s. Although it was somewhat time consuming to produce pellets in this manner, this produce ensured pellets with consistent density, form and size (10 mm diameter and 8 mm height), which allowed for the subsequent monovariance investigation of the pelletised thermally pre-treated CTP samples.

2.2.3. TMA analysis

A single thermally pre-treated CTP pellet (prepared according to Section 2.2.2) was placed in a Seiko Instruments Inc. TMA/SS 6100, interfaced with SII EXSTAR 6000. With this instrument, the dimensional changes of the pellet could be measured as a function of temperature. The TMA was programmed to heat the pellet from room temperature up to 800 °C at a rate of 10 °C/min, under a constant N_2 flow of 1.7 NL/min. An inert atmosphere was maintained, as the oxidation of the pre-treated CTP sample had to be prevented. This procedure was repeated three times for each sample pre-treatment at a specific temperature. Each TMA curve presented in this paper is the average determined from these repetitions.

2.2.4. FTIR spectroscopy analysis

The qualitative investigations of the different functional groups in the as-received CTP, as well as the CTP samples thermally pre-treated, were performed using a Perkin Elmer Spectrum 400 FT-IR/FT-NIR equipped with a universal attenuated total reflectance (ATR) sampling accessory. The FTIR spectra for all raw and thermal treated samples were recorded in the range of 4000–650 cm^{-1}.

3. Results and discussion

3.1. As-received CTP sample characterisation

The proximate and ultimate analyses, as well as the fundamental properties of the as-received CTP samples are summarised in Tables 1 and 2, respectively. As can be seen, the characteristics of the obtained CTP samples varied considerably, e.g. volatiles: 51.4–69.8%, FC: 29.1–48.2%, SP: 65.4–134.2 °C, CV: 37.1–60.3%, QI: 2.9–7.3% and TI: 16.0–34.6%. This spread in characteristics is larger than reported in most previous studies related to CTP (Diaz and Blanco, 2003; Guillen et al., 1996; Panaitescu and Predeanu, 2007; Machnikowski et al., 1997). CTP samples with such different characteristics were obtained intentionally from the various suppliers, as it was the intention to test the hypothesis put forward in the paper by evaluating CTP samples that differ as much as possible.

3.2. Determination of the baking isotherm temperature of Söderberg electrodes

In order to investigate the baking isotherm temperature, the CTP samples were thermally pre-treated (as described in Section 2.2.2) at temperatures ranging from 400 to 500 °C, with increments of 25 °C. The measured dimensional changes of these thermally pre-treated CTP pellets indicated that pellets prepared from all the CTP samples softened during the TMA analysis, if the thermal pre-treatment temperatures $\leqslant$450 °C. This softening was indicated by a sudden change in the dimensional behaviour of the thermally pre-treated pelletised CTP samples during TMA analysis as the temperature increased. Typical examples (CTP 1–6) of this softening behaviour observed during the TMA are indicated in Fig. 2. As can be seen from the data presented in Fig. 2, sample softening was indicated by a sudden decrease in dimension for some samples. However, other samples expanded due to softening. This was due to the core of the pellet melting and running out the bottom of the pellet, thereby causing the TMA instrument to measure an increase in size. All of these softening behaviours were, however, characterised by a very sudden change in pellet dimension. CTP samples 6–12 reacted similarly, but are not shown in Fig. 2 to prevent the figure from becoming too crowded.

In contrast to the above-mentioned results, none of the pelletised thermally pre-treated CTP samples indicated any softening behaviour, when the pre-treatment temperature was $\geqslant$475 °C.

Table 1
Proximate and ultimate analyses of the as received CTP samples.

Sample	Proximate analysis				Ultimate analysis				
	Moisture (%)	Volatiles (%)	Ash (%)	FC (%)	C (%)	H (%)	N (%)	S (%)	O (%)
CTP 1	0.2	55.6	0.4	43.8	90.80	4.16	1.15	0.49	3.40
CTP 2	0.6	69.8	0.5	29.1	91.54	4.13	1.17	0.49	2.67
CTP 3	0.7	65.2	0.7	33.4	91.98	4.03	1.13	0.53	2.33
CTP 4	0.2	63.6	0.4	35.8	90.72	4.23	1.19	0.53	3.33
CTP 5	0.3	63.4	0.5	35.8	91.27	4.36	1.17	0.53	2.67
CTP 6	1.0	62.8	0.9	35.3	90.32	4.33	1.25	0.55	3.55
CTP 7	0.6	69.0	0.8	29.6	91.43	4.12	1.15	0.50	2.80
CTP 8	0.2	51.4	0.2	48.2	93.38	3.23	1.15	0.50	1.74
CTP 9	0.2	64.3	0.3	34.9	91.38	4.35	1.14	0.50	2.63
CTP 10	0.2	59.5	0.6	39.7	91.23	3.89	1.16	0.49	3.23
CTP 11	0.1	60.7	0.5	38.7	91.01	4.19	1.18	0.50	3.12
CTP 12	0.1	58.1	0.5	41.3	91.06	3.85	1.17	0.53	3.39

Table 2
Fundamental properties of the as received CTP samples.

Sample	SP (°C)	CV (%)	QI (%)	TI (%)
CTP 1	121.2	56.9	6.6	26.3
CTP 2	81.9	37.1	3.6	16.0
CTP 3	66.5	37.2	3.7	16.2
CTP 4	94.1	46.8	4.5	20.0
CTP 5	94.6	47.5	4.6	19.1
CTP 6	95.6	41.5	3.8	20.0
CTP 7	82.6	47.6	5.4	24.0
CTP 8	134.2	60.3	7.0	34.6
CTP 9	83.1	43	2.9	23.7
CTP 10	93.8	50.0	5.8	18.2
CTP 11	65.4	46.6	7.3	22.2
CTP 12	85.0	48.7	7.2	23.2

Typical TMA curves of samples pre-treated at 475 °C are indicated in Fig. 3. Again, only six samples (CTP 1–6) were selected for illustration purposes, since the other samples reacted similarly. In contrast to the pre-treated samples that indicated softening behaviours, which was indicated by sudden dimensional changes, these samples exhibited gradual dimensional changes.

The fact that none of the pelletised pre-treated CTP samples softened when the thermal pre-treatment temperature was 475 °C, indicates that solid carbonaceous material is formed between 450 and 475 °C. By comparing the TMA thermal behaviour of the pellets prepared from CTP thermally pre-treated at maximum temperatures in the range of 400 to 450 °C and those that were pre-treated at a maximum temperature of 475 °C, it can be deduced that the baking isotherm temperature of CTP used as a binder in Söderberg electrodes lies between 450 and 475 °C. It is acknowledged that the thermal behaviour of the mixture of filler (e.g. calcined anthracite or coke) and binder (CTP) in Söderberg electrode paste might differ from the characteristics of the CTP used as a binder, but the softening behaviour of the paste is likely to be linked to the CTP rather than the filler.

Beukes et al. (2013), who developed the TMA method employed in this study, also reported the baking isotherm temperature of two CTP samples to be between 450 and 475 °C. However, since these authors (Beukes et al., 2013) only considered two case study CTP samples, they could not deduce with certainty that this would be valid for other CTPs. Considering the vast differences in the chemical composition (Table 1) and fundamental properties (Table 2) of the CTP samples considered in this paper, it was somewhat surprising to find that the baking isotherm temperatures of all the CTP samples evaluated were between 450 and 475 °C. However, the results led the authors to believe that although there might be differences in the chemical composition and fundamental properties of the untreated CTP samples (Tables 1 and 2), the inert atmosphere heat treatment led to the loss of organic compound with similar functional groups from all the CTP samples, resulting in the formation of a solid carbonaceous matrix not including some of these organic compound functional groups. This implies that the temperature of the Söderberg electrode paste baking isotherm is independent of the initial chemical composition and the fundamental properties of the CTP (Table 1). In order to prove/disprove this hypothesis, FTIR analyses of the as-received CTP samples, as

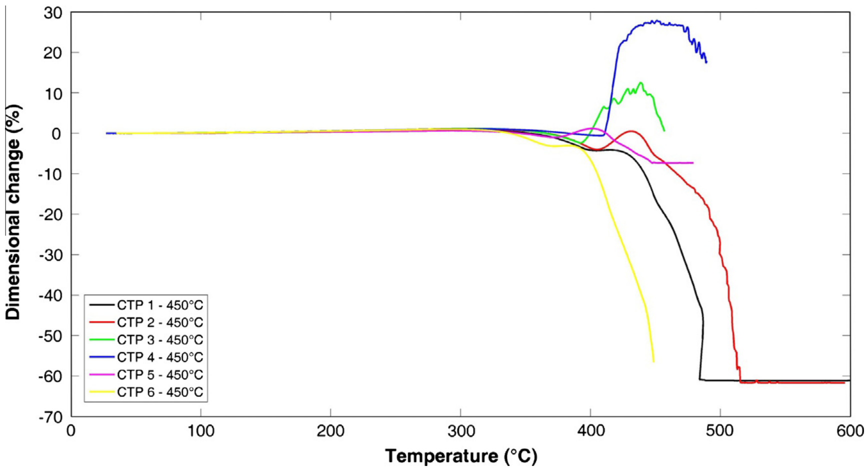

Fig. 2. Typical softening behaviour observed during TMA for CTP samples thermally pre-treated at ⩽450 °C.

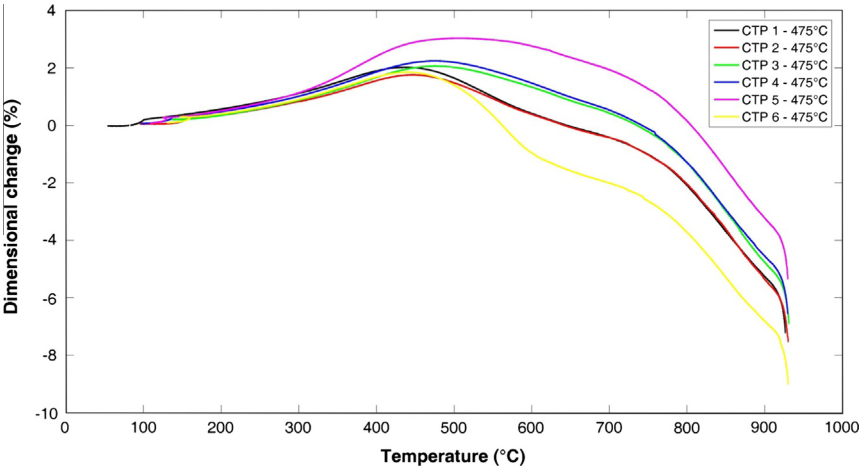

Fig. 3. Dimensional behaviour during TMA for CTP samples thermally pre-treated at 475 °C.

well as the CTP samples pre-treated at 475 °C, were conducted to determine the organic functional groups present in the samples.

3.3. FTIR analysis

FTIR analysis determines the different functional groups in a sample by considering the characteristic bands of the C—H structure. In this study, FTIR analysis was performed on all 12 raw (as-received) CTP samples. Fig. 4 indicates the FTIR spectra of CTP 1–6, respectively. The FTIR spectra of the remaining six CTP samples exhibited peaks at the same wave numbers with the only difference being the intensities of the different peaks. This FTIR data implies that all the raw CTP samples contained organic compounds with similar functional groups (indicated by similar wave numbers of the peaks/bands), with the only difference being the fractional distribution of these compounds in the different CTP samples (indicated by the peak intensities).

Although it is very difficult to quantify the occurrence of different functional group compounds occurring in the CTP samples from the FTIR spectra, a qualitative explanation of the observed bands can be provided. The FTIR band at 3412 cm^{-1} is an indication of the presence of N—H and O—H groups; 3040 cm^{-1} confirms the existence of aromatic bands showing some unsaturation. Peaks at 2970–2850 cm^{-1} confirm the presence of alicyclic and aliphatic CH_3, CH_2 and CH. The 1699 cm^{-1} peak is characteristic of C═O and aromatic C═C. Peaks at 1436 cm^{-1} are due to CH_3 asymmetric deformations and CH_2 groups in bridges, which may be due to aromatic C═C and strongly bonded OH. The band in the region of 880–750 cm^{-1} is an aromatic stretch (Guillen et al., 1995; Prauchner et al., 2001, Guillen et al., 1992).

Since the baking isotherm temperatures of all 12 CTP samples considered were found to be between 450 and 475 °C, the FTIR spectra of all CTP samples thermally pre-treated at 475 °C were also recorded. Fig. 5 presents the FTIR spectra of CTP 1 to CTP 6 that have been thermally pre-treated at 475 °C, respectively. Again, only the FTIR spectra of the first six CTP samples were shown, to avoid overcrowding of the figure.

From Fig. 5 it is evident that the FTIR spectra obtained for the various samples thermally pre-treated at 475 °C are similar. These spectra are also typical of carbonaceous materials (Guillen et al., 1995). If the spectra of these thermally pre-treated CTP samples are compared to the FTIR spectra of the raw CTP samples (Fig. 4), it is clear that a reduction in some functional groups occurred, as well as the formation of new groups characterised by significant peaks in the region 2400–1900 cm^{-1}. The compounds in this band could not be identified, as the authors were unable to find literature indicating the possible nature of functional groups with peaks in this region. The bands in the region of 3896–3442 cm^{-1} could be assigned to N—H stretching (Guillen et al., 1992, 1995). 3050 cm^{-1} and the weak peak at 2923 cm^{-1} could be assigned to aromatic and aliphatic C—H stretching (Strydom et al., 2011). Bands in the region ranging from 700 to 900 cm^{-1} were assigned to out-of-plane aromatic compounds (Papole et al., 2012). Peaks at 1436 cm^{-1} are due to CH_3 and CH_2 linkages (Guillen et al., 1992, 1995). Peaks

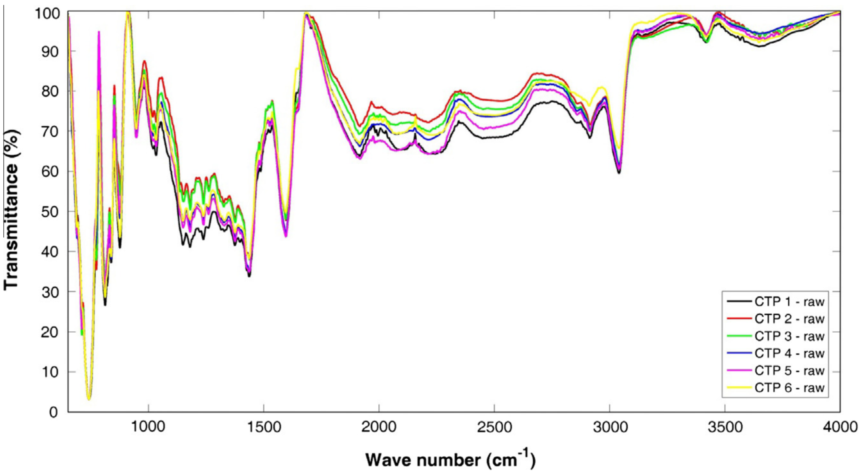

Fig. 4. FT-IR spectra of raw coal tar pitch samples.

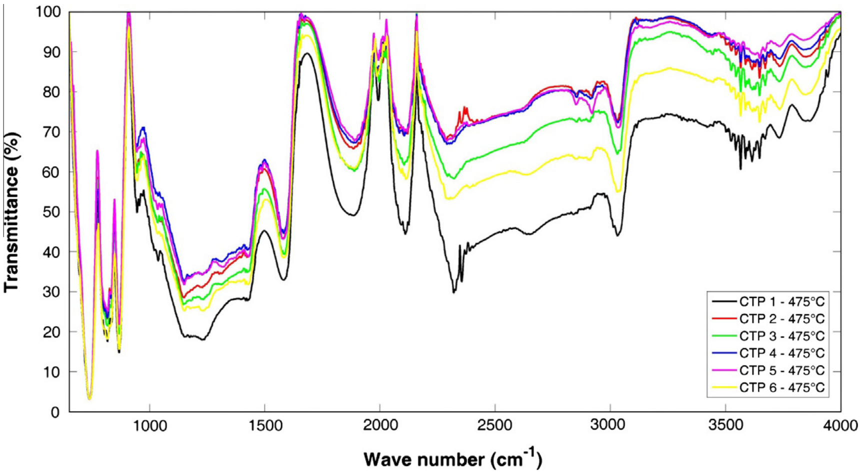

Fig. 5. FTIR spectra of coal tar pitch samples pre-treated at 475 °C.

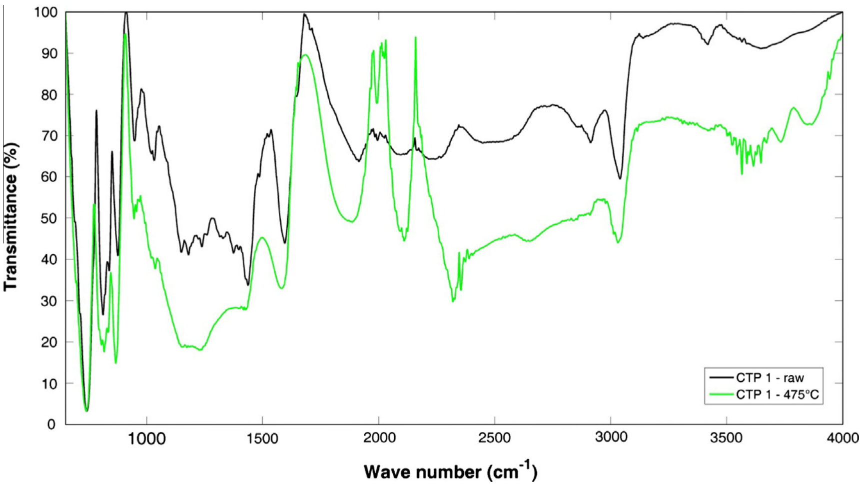

Fig. 6. Comparison of FTIR spectra of raw and thermally pre-treated CTP samples.

at 1597 cm^{-1} are due to carbonyl compounds, as well as aromatic C=C. The peak at 1253 cm^{-1} is due to aryl ethers, aryl oxygen (Ibara et al., 1989), with bands at 1173 and 1065 cm^{-1} being assigned to clay minerals. During the thermal treatment of coal tar pitch, polymerisations and thermal degradation reactions take place. This leads to a loss of some functional groups as they are converted into volatile components, which are released during thermal treatment (Yue and Watkinson, 1998). Therefore, a reduction in the peak intensities of some identified functional groups in thermal treated pitch samples takes place.

In order to visualise the differences between the FTIR spectra of the raw and thermally pre-treated CTP samples at 475 °C, the FTIR spectra of a raw and 475 °C pre-treated CTP sample are shown in Fig. 6. These specific samples were chosen since the peak intensities at approximately 3000 cm^{-1} were almost the same, which helps to identify significant differences.

4. Conclusion

The data presented in this paper confirms that TMA is a useful tool to assess the dimensional behaviour of CTP samples. Thermal pre-treatment and subsequent TMA analysis indicated that the baking isotherm temperature of CTP used in Söderberg electrodes lies between 450 and 475 °C. It was found that this temperature is independent of the initial physical and chemical composition of the CTP. As far as the authors could assess, this is a novel finding, which could help operational personnel at smelters utilising Söderberg electrode systems to manage their electrodes better. A better defined temperature range for the baking isotherm temperature will allow more precise electrode management; and therefore lead to improved operational stability and reduced safety risks. These findings also provide researchers with new questions that need to be answered to better understand these complex systems.

Although FTIR analysis could not be used to quantify the different functional groups in the CTP samples, it indicated that the raw CTP samples were similar in composition, only differing in terms of the fractional composition of the various functional group compounds. The 475 °C pre-treated CTP samples also had similar FTIR spectra, but these spectra differ somewhat from that of the raw CTP samples. This indicates that the organic functional groups present in the CTP samples changed as a result of the thermal pre-treatment. This also implies that similar functional group compounds are lost and new ones formed during the transition of a molten CTP to a solid carbonaceous material, irrespective of the initial composition of the CTP.

As a future perspective, more research into this field should be encouraged, especially to quantify the chemical differences between raw CTP and CTP that have been transformed into solid carbonaceous material due to thermal treatment.

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References

Beukes, J.P., Roos, H., Shoko, L., Van Zyl, P.G., Neomagus, H.W.J.P., Strydom, C.A., Dawson, N.F., 2013. The use of thermomechanical analysis to characterise Söderberg electrode paste raw materials. Minerals Engineering. accepted for publication.

Diaz, C., Blanco, C.G., 2003. NMR: a powerful tool in the characterization of coal tar pitch. Energy and Fuels 17, 907–913.

Fitt, A.D., Aitchison, J.M., 1993. Determining the effective viscosity of a carbon paste used for continuous electrode smelting. Fluid Dynamic Research 11, 37–59.

Guillen, M.D., Dominguez, A., Iglesias, M.J., Blanco, C.G., 1992. Semi quantitative FTIR analysis of a coal tar pitch and its extracts and residues in several organic solvents. Energy and Fuels 6 (4), 518–525.

Guillen, M.D., Iglesias, M.J., Dominguez, A., Blanco, C.G., 1995. Fourier transform infrared study of coal pitches. Fuel 74 (11), 1595–1598.

Guillen, M.D., Dominguez, A., Iglesias, M.J., Fuente, E., Blanco, C.G., 1996. Analysis of coal tar pitch: relations between thermal behavior and composition. Fuel 75 (9), 1101–1107.

Ibara, J.V., Cervero, I., Moliner, R., 1989. Structural characterization of low temperature pyrolysis tars and their relation with parent coals. Fuel Processing Technology 2 (2), 135–149.

Innvaer, R., 1989. The Söderberg electrode system recent research and development new challenges. In: Proceedings: Infacon, 5th International Congress, April 23–26, New Orleans, Louisiana.

Innvaer, R., Olsen, L., 1980. Calculation of thermal stresses in Söderberg Electrodes. In: Proceedings: International Union for Electro Heat (UIE), 9th International Congress, Cannes, pp. 2–11.

Innvaer, R., Olsen, L., Vatland, A., 1984. Operational parameters for Söderberg electrodes from calculations, measurements and plant experience. In: Proceedings: Mintek, vol. 50, pp. 787–797.

Kleynhans, E.L.J., Beukes, J.P., Van Zyl, P.G., Kestens, P.H.I., Langa, J.M., 2012. Unique challenges of clay binders in a pelletized chromite pre-reduction process. Minerals Engineering 34, 55–62.

Machnikowski, J., Machnikowska, H., Diez, M.A., Alvarez, R., Bermejo, B., 1997. Characterization of coal derived pitches as precursors for advanced carbon materials chromatographic and related techniques. Journal of Chromatography A 778, 403–413.

Mason, C.R., 1970. Correlations between pitch binder properties and properties of Söderberg electrodes. Fuel 49 (2), 165–174.

McDougall, I., Smith, C.F.R., Olmstead, B., Gericke, W.A., 2004. In: Proceedings: Infacon, 10th International Ferroalloys Congress. February 1–4, Cape Town, South, Africa, pp. 575–584.

Meyjes, R.P., Venter, J., van Rooyen, U., 2010. Advanced modelling and baking of electrodes. In: The Twelfth International Ferroalloys Congress, June 6–9, Helsinki, Finland, pp. 779–788.

Monge, J.A., Amoros, D.C., Solano, A.L., 2001. Characterization of coal tar pitches by thermal analysis, infrared spectroscopy and solvent fractionation. Fuel 80, 41–48.

Neizel, B.W., Beukes, J.P., Van Zyl, P.G., Dawson, N.F., 2013. Why if $CaCO_3$ not used as an additive in the pelletised chromite pre-reduction process? Minerals Engineering 45, 115–120.

Nel, V.A., Strydom, C.A., Schobert, H.H., Beukes, J.P., Bunt, J.R., 2011. Comparison of sintering and compressive strength tendencies of a model coal mineral heat-treated in inert oxidizing atmospheres. Fuel Processing Technology 92 (5), 1042–1051.

Nelson, L.R., Prins, F.X., 2004. Insights into the influences of paste additions and levels on Söderberg electrode management. In: Proceedings: Infacon 2004, Tenth International Ferroalloys Congress; February 1–4, Cape Town, South Africa, pp. 418–431.

Panaitescu, C., Predeanu, G., 2007. Microstructural characteristics of toluene and quinoline- insolubles from coal-tar pitch and their cokes. International Journal of Coal Geology 71, 448–454.

Papole, G., Focke, W.W., Manyala, N., 2012. Characterization of medium-temperature Sasol-Lurgi gasifier coal tar pitch. Fuel 98, 243–248.

Prauchner, J.M., Pasa, V.M.D., Otani, C., Otani, S., 2001. Characterization and thermal polymerization of eucalyptus tar pitches. Energy and fuels 15, 449–454.

Roos, H., 2011. Thermomechanical analysis of raw materials used in the production of Soderberg electrode paste. MSc thesis. North West University.

Sem, M.O., 1954. The Soderberg self-baking electrode. Journal of The Electrochemical Society 101 (10), 487–492.

Strydom, C.A., Bunt, J.R., Schobert, H.H., Raghoo, M., 2011. Changes to the functional groups of an inertinite rich medium rank bituminous coal during acid treatment processes. Fuel Processing Technology 92, 764–770.

Walker, L., 1986. Coal derived carbons. Carbon 24 (4), 379–386.

Yue, C., Watkinson, A.P., 1998. Pyrolysis of pitch. Fuel 77 (7), 695–711.