Asian Journal of Chemistry Vol. 18, No. 2 (2006), 982–990

Effect of Temperature on the Efficiency of the Thermal Cell

WALEED M. SARHAN†, AHMED N. ALKHATEEB‡, KAREEM D. OMRAN and FALAH H. HUSSEIN*
Department of Chemistry, College of Science for Women, Babylon University, Iraq
E-mail: abohasan_hilla@yahoo.com

The operational temperature of the laboratory thermal cell was found to be within the range 455–460°C, at which the alloy, $CaLi_2$ was formed, which led to the oxidation of the calcium anode and the release of the electrons. The effect of different temperatures upon the efficiency of the thermal cell at different times has been studied. The results show that 460°C is the most appropriate temperature, where a regular discharge took place beside the generation of the most stable voltage. This result is explained as being due to the fast assimilation of the reactants. Concerning the assembled thermal cell, the operation temperature was determined to be 455–460°C, which is identical with that found with the laboratory thermal cell. An obvious increase of the voltage to become 2.3 V, which was regularly formed, has been observed. Moreover, studying the effect of the same temperatures, used with the laboratory thermal cell, that is 400, 460 and 520°C, has been carried out. It revealed that 460°C represents the optimum temperature for the assembled thermal cell to work with the highest efficiency, where the molten salt, depolarizer and the binder were LiCl-KCl, $CaCrO_4$ and SiO_2, respectively.

Key Words: Temperature, Effect, Efficiency, Thermal cell.

INTRODUCTION

Thermal batteries are power sources with high power densities[1]. Environmentally, they are very safe because they do not leak any toxic or harmful materials. Disposed thermal batteries contain no cadmium or lead and do not give rise to any significant disposal or environmental problem[2]. They are especially useful for supplying short-term power in disposable weapons (*e.g.*, torpedoes and projectiles) and exploratory spacecraft, such as "Spirit" and "Opportunity" rovers, which touched down and explored opposite sides of Mars in 2004. Both rovers used lithium primary batteries beside the rechargeable batteries[3].

The thermal battery active materials and especially the electrolyte are solid and nonconductive at ambient temperature. They remain inert before activation; thus they have a long shelf-life of more than 20 years, until brought into use and

†Chemistry Department, College of Science, Kufa University, Iraq.
‡Chemistry Department, College of Science, Ibb University, Yemen.

activated at once, by supplying an energy pulse from an external source, which initiates the thermal battery and ignites the pyrotechnic substances to melt the electrolyte, which becomes conductive and allows ionic migration, required to afford the electrical charge. The activation time ranges from 0.1–1 s. Thereafter, the battery remains active for as long as 1 h or only a few seconds, depending upon several factors such as its size, the thermal insulation and the electrochemical system[1]. Thermal batteries frequently utilize a molten LiCl-KCl mixture as the electrolyte. Several cathodes can be employed including metal oxides and sulfides, $PbCrO_4$, $CaCrO_4$, K_2CrO_4 and $K_2Cr_2O_7$. However, lithium/iron disulfides have several advantages over the others, including the high stability in extreme dynamic environments, easily constructed, large current ability and high performance. These characteristics render these batteries the most widely used. Moreover, the lithium/cobalt disulfide provides better stability at high temperatures owing to its steadiness to 650°C. The most common anode used is lithium, though magnesium and calcium are also utilized. Lithium batteries represent one of the most highly active batteries. Lithium has atomic mass, is extremely reactive and has the highest amp-hour capacity of all metals in the periodic table. These attributes have renderred lithium metal an attractive anodic material in thermal batteries during the past thirty years[4].

Concerning the effect of temperature on the efficiency of the thermal battery and in a comparative study between the two thermal cells, Ca | LiCl-KCl | $PbSO_4$ and Mg | LiCl-KCl | $PbSO_4$, Styczynski *et al.*[5] studied the relation between capacity discharge and the temperatures ranging from 400–650°C for the Ca anode and from 400–550°C for the Mg cathode, using electrolytes of the composition shown in Table-1 and cathodes having the composition revealed in Table-2.

TABLE-1
COMPOSITION OF DIFFERENT ELECTROLYTES APPLIED INTO THE CELLS

	E-I (%)	E-II (%)	E-III (%)	E-IV (%)	E-V (%)
LiCl	25	44	50	56	35
KCl	75	56	50	44	65

TABLE-2
COMPOSITION OF DIFFERENT CATHODIC MASSES APPLIED INTO THE CELLS

	K-I (%)	K-II (%)	K-III (%)	K-IV (%)	K-V (%)
$PbSO_4$	50	50	50	50	50
LiCl	22	15	25	28	35
KCl	28	35	25	22	15

With the Ca cell composed of the cathodes K-I to K-V and an invariable electrolyte E-I, the results showed that the cathode K-V offered the highest discharge capacities almost through the whole mentioned temperature range. The best temperature was 550°C, which gave the maximum discharge capacity of 137 As.

Keeping the Ca cathode invariable of K-V composition, whereas the electrodes composition ranging from E-I to E-V, it was demonstrated that E-I gave the highest discharge capacity of 140 As at 550°C.

With the Mg cell composed of the cathodes K-I to K-V and an invariable electrolyte E-I, it was obtained that all the cathodes except K-II showed very similar dependence on the mentioned temperature range. Using the K-II cathode gave rise to the displacement of efficient work range of cells towards higher temperatures, where the maximum discharge capacity of 150 As at 550°C was obtained.

Keeping the Mg cathode invariable of K-V composition, whereas the electrodes composition ranged from E-I to E-V, E-I gave the highest discharge capacity of 138 As at 425°C.

EXPERIMENTAL

All the utilized chemicals were purchased from BDH, E-Merck or Fluka, with purities > 95% and utilized as supplied. Preparation of the molten salts as well as storing the components of the thermal cell were performed inside a dry box flushed with argon.

Techniques

All the experimental techniques 1–5, mentioned below, have been fully described previously[6]:

1. **Construction of the glass cell.**
2. **The preparation of molten salts.**
3. **Determination of the weight percentage ratio for the depolarizer.**
4. **Operation of the thermal cell.**
5. **The thermal analysis.**
6. **Effect of temperature upon the voltage of the laboratory thermal cell:** The effect of temperature upon the voltage of the cell, which was operated inside the furnace, was studied by connecting the cell to a voltmeter and monitoring the change of voltage with time after raising the temperature up to 400°C. The experiment was repeated at 460 and 520°C. In each case, the voltage variation with time was recorded.
7. **The optimum temperature for the operation of the assembled thermal cell:** The optimum temperature was determined as follows: the assembled thermal cell was insulated, connected to a voltmeter and moved on a glass slide inside the furnace. The temperature was gradually raised from 200–620°C. The temperatures and their correspondent voltages were recorded. The process was repeated two times to obviate the mistakes resulting from the change of cell assembling conditions.
8. **Effect of temperature upon the voltage of the assembled thermal cell:** The effect of temperature upon the voltage of the assembled thermal cell operated inside the furnace was investigated *via* monitoring the voltage changes resulting

from varying the temperature of the thermal cell. The cell was insulated, joined to a voltmeter and followed by increasing gradually the temperature up to 400°C. The experiment was repeated at 460 and 520°C. At all times, the variation of voltage with time was recorded.

RESULTS AND DISCUSSION

The components of the thermal cell

The components of the thermal cell including the Ca and Mg anodes, the cathode which is composed of the depolarizers (D): $CaCrO_4$, $K_2Cr_2O_7$ or K_2CrO_4, the electrolyte (E): LiCl-KCl and binder (B): SiO_2 were previously fully described[6]. In addition, thermal analysis of the electrolyte in the absence and presence of the depolarizers has been investigated before[6].

The operation temperature of the laboratory thermal cell

Fig. 1 represents a study aiming to recognize the temperature at which the laboratory thermal cell gives the maximum voltage. It was observed that the cell works with a maximum efficiency at 455–460°C, where the voltage is 0.78–0.80 V. Every thermal cell system has an operating temperature, at which the best ability of the reactants to generate the energy takes place with invariable electrical discharge[7]. To recognize the temperature at which the cell gives the maximum voltage, the cell was put inside the furnace. The temperature was raised from 150–600°C, where an obvious fast rising in the voltage was noticed after 350°C.

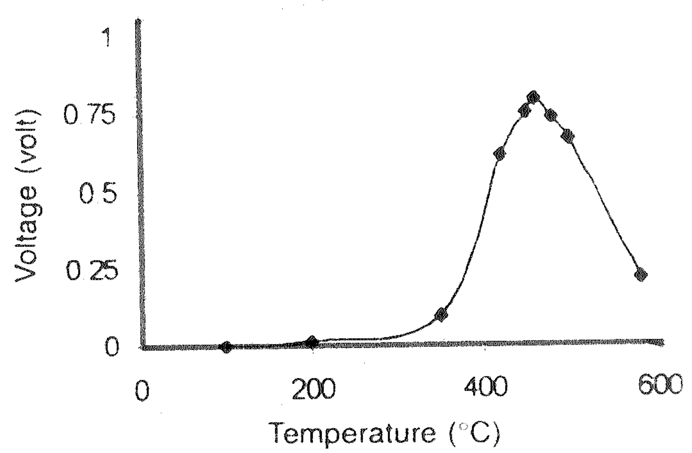

Fig. 1. The operating temperature of the laboratory thermal cell

This is a very important distinguishable property for these systems, especially in the aerial applications, where the main aim is to generate a high voltage in a very short time[8]. Concerning the laboratory cell, the increase in the voltage started with 400°C, at which the voltage was 0.45 V, which was 0.098 V at 350°C. This is explained as being due to the formation of the alloy[9], $CaLi_2$, where the melting of Ca in the presence of the electrolyte, LiCl, gave rise to the formation of the alloy. Therefore, this alloy oxidized Ca to release electrons. Fig. 1 also demonstrates that the maximum voltage was generated between 455–460°C. After this range a decrease in the maximum voltage was noticed, which was referred to the shortest electrode's surface area as well as the non-homogeneous partition of electrons between the electrodes. The voltage started descending down to 0.002 V, inasmuch as the rise of temperature results in the consumption of the active reactants inside the thermal cell[10].

Effect of temperature upon the voltage of the laboratory thermal cell

Figs. 2–4 reveal the great effect of the temperatures 400, 460 and 520°C, with time, upon the laboratory thermal cell voltage, respectively. Raising the temperature promoted the activity of the electrolyte due to the increment of the solubility of the molten salts[11]. Fig. 2 shows that at 400°C, when approaching the voltage of 0.001 V, the cell age approached 9.5 min. Fig. 3 demonstrates that at 460°C, which was the operation temperature, the discharge was regular and the generated voltage was more stable than that at 400°C. The operation age of the cell was 5.5 min. This regularity was referred to the stable rate of assimilation for the efficacious materials inside the cell. This result may be attributed to the increment in the solubility of the depolarizer, $CaCrO_4$, into the electrolyte, which led to the regular consumption of the cell. Fig. 4 reveals that at 520°C, a disturbance in the curve of cell self-discharge took place. Here, elevation of the temperature increased the reaction rate, which gave rise to the exaggerated formation of the alloy, $CaLi_2$. This alloy may insulate the anode to slow down the reactions, which dissociate the alloy, thus releasing the electrons. Therefore, a depressed voltage resulted. It is believed that the alloy created a thin layer around the anode in the thermal cell[12]. The lifetime of this cell at 520°C was 2.5 min. The cell was unstable, its consumption time was highly less than its counterparts and the produced voltage approached 0.91 V. This was attributed to the increase in the temperature, which raised the rate of the electrochemical reaction and therefore lowered the cell age. Moreover, it could be concluded that raising the temperature led to the increase of the rate of reactions, which consumed the active materials in the cell. In addition, it was deduced that the depolarizer enhanced the activity of the cell through the reduction of the polarization. Also, it is possible that the excessive formation of CaLi2 alloy diminished the voltage.

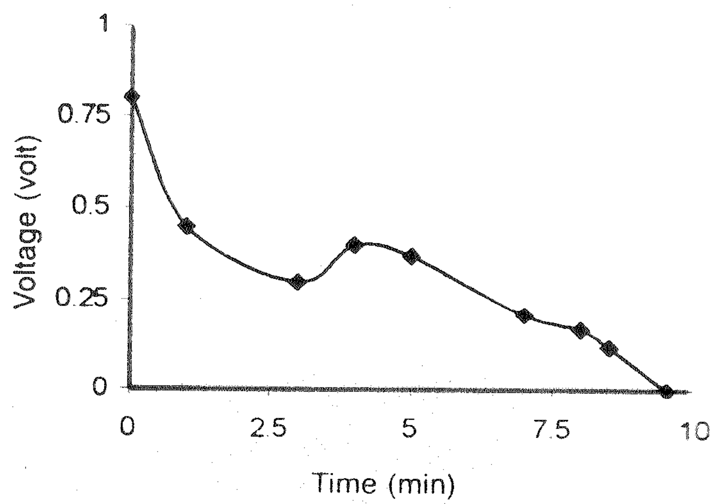

Fig. 2. Variation of voltage with time at 400°C for the laboratory cell

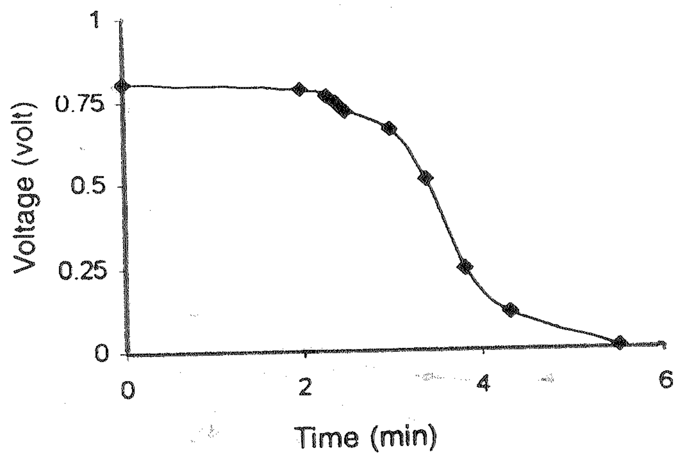

Fig. 3. Variation of voltage with time at 460°C for the laboratory cell

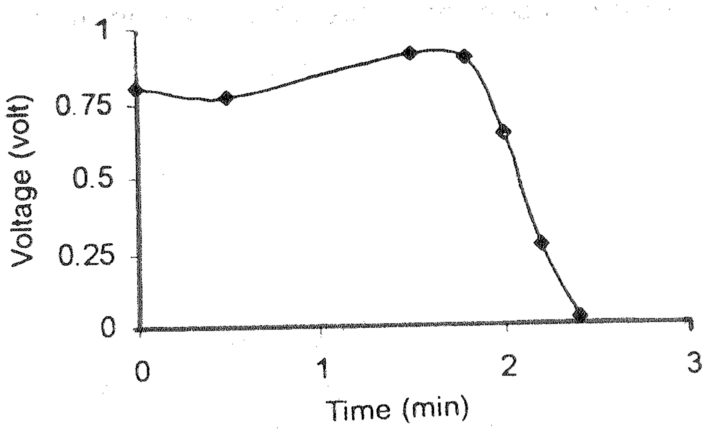

Fig. 4. Variation of voltage with time at 520°C for the laboratory cell

The operation temperature for the assembled thermal cell

Fig. 5 illustrates the investigation carried out to recognize the operating temperatures for the assembled thermal cell, which was constructed after the press of the discs. The study has been performed, utilizing the thermal furnace, to provide the thermal conditions required for the operation of the cell. It was noticed that the operating temperature for the thermal cell was within the range 460–465°C, which was identical with that of the laboratory cell. In addition, it was observed that the voltage generation process was more regular with an obvious increase in the voltage to reach 2.3 V. This was explained as being due to the alteration of the surface of electrodes as well as the increment in the thermal electrolyte conduction resulting from the regular distribution of the molten salt.

The active cells systems, due to their containment of thermal materials, should operate within a range that gives the best activation of the thermal cells to operate with the same efficiency[13].

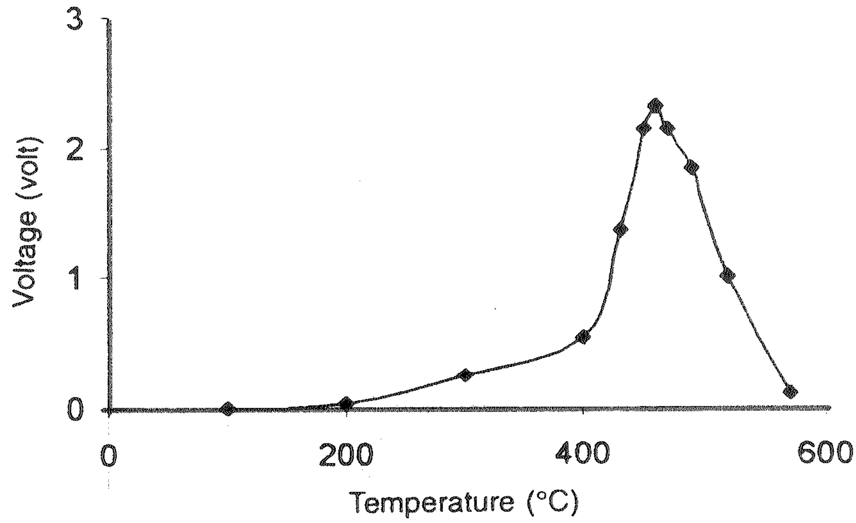

Fig. 5. The operation temperature for the assembled thermal cell

Effect of temperature upon the voltage of the assembled thermal cell

Figs. 6–8 demonstrate the effect of the temperatures 400, 460 and 520°C on the voltage of the assembled thermal cell, respectively. Fig. 6 shows that after 10 min of putting the thermal cell at 400°C, a decline of the voltage from 2.3 V to 1.25 V took place. Thereafter, a depression in the voltage to 0.04 V was identified after 130 min. The long period of operation for this cell is believed to be due to the incomplete solubility of $CaCrO_4$ at this temperature and consequently the rates of the thermochemical reactions becoming slower. This led ultimately to the elongation of the operation period for the thermal cell, where the Ca electrode was less consumed compared with other cells, which had low activities.

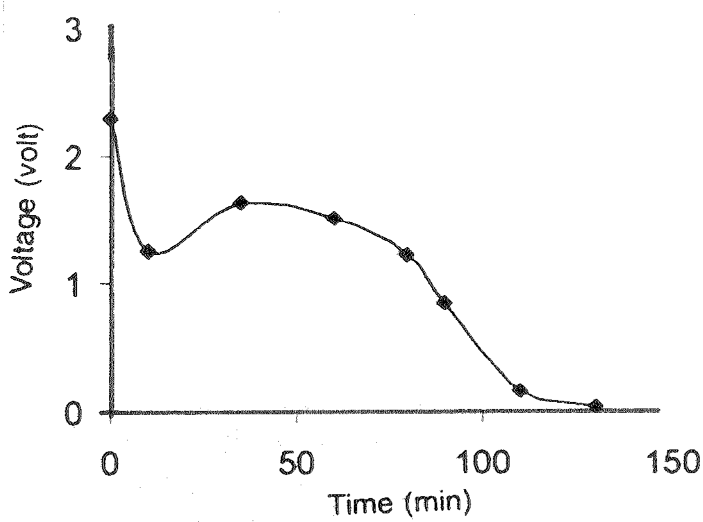

Fig. 6. Variation of voltage with time at 400°C for the assembled cell

It is clearly noticed from Fig. 7 that the temperature, 460°C, gave a higher voltage 2.3 V, at lower time than that at 400°C. This result is a consequcnce of accelerating the thermochemical reactions, with raising the temperature by 60°C, which decreased the operation period for the cell, which ended at 90 min. In addition, it is observed from the same figure that after 10 min, the voltage was reduced to 2.24 V and then to 1 V after 60 min. The voltage continued to descend until 0.011 V after 90 min from the operation commencement.

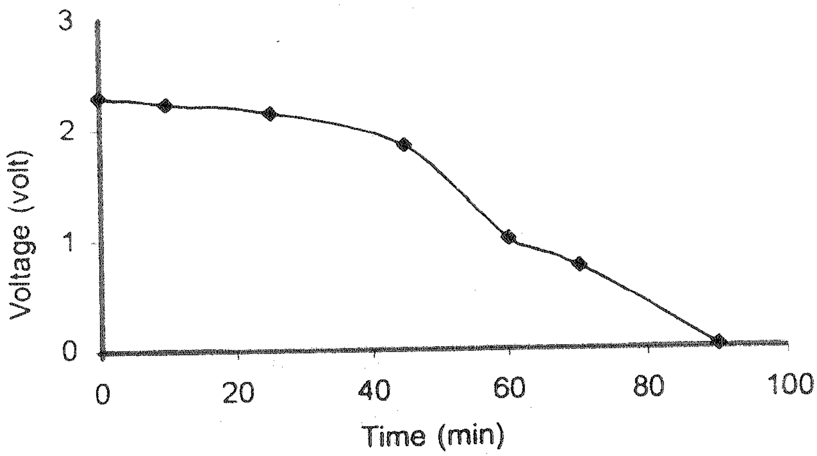

Fig. 7. Variation of voltage with time at 460°C for the assembled cell

Fig. 8 discloses the effect of temperature, 520°C, upon the voltage of the produced thermal cell, where the voltage became 2.41 V. However, The cell suffered from the irregular electrical discharge, where the voltage went down after 5 min to 2.12 V to ascend to 2.41 V and declined once again to 2.23 V within 15 min from the beginning of operation. The activity time was only 45 min, which was referred to the hastening of the reaction that caused the consumption of the effective materials inside the cell and consequently reduction of the cell operation time.

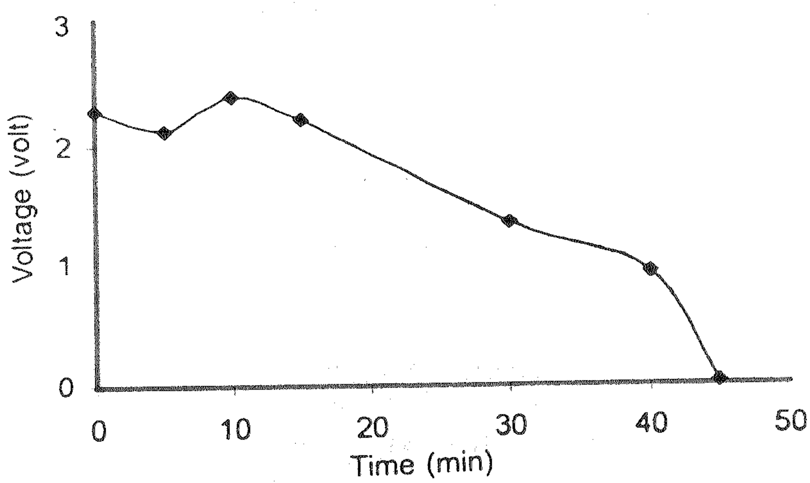

Fig. 8. Variation of voltage with time at 520°C for the assembled cell

From the above mentioned comparison, it is obviously demonstrated that the temperature 460°C represented the optimal temperature for the operation of the assembled thermal cell, where a molten salt of $CaCrO_4$, a binding material of SiO_2 and Ca was the anode. It is of high necessity to reach this temperature, *i.e.*, 460°C, at the ordinary operational conditions for the running of the thermal cell with the highest efficiency.

REFERENCES

1. G. Portal, E. Euvrad, P. Tailhades and A. Rousset, *Powder Metallurgy*, **42**, 34 (1999).
2. D.M. Ryan, American Institute of Aeronautics and Astronautics, Washington (1993).
3. S. Surampudi, The Electrochemical Society Interface, 22 (Spring 2004).
4. M.A. Zafar, US Pat. 6,627,353 (September 30, 2003).
5. S. Styczynski, S. Tabat, Z. Brudka, B. Olejnik and A. Ciszewski, Effect of Temperature, Cathode Material and Electrolyte Composition on the Operation of Thermal Cells, 51st ISE Meeting, Warsaw, Poland (2000).
6. W.M. Sarhan, A.N. Alkhateeb and F.H. Hussein, *Asian J. Chem.*, **18**, 397 (2006).
7. R. Ubbelohde and S.E. Rogers, Brit. Pat. 3,865,810 (April 19, 1961).
8. H.A. Latininen, R.P. Tisher and D.K. Roe, *J. Electrochem. Soc.*, **107**, 555 (1960).
9. G.S. Smith, Storage Batteries, 3rd Edn., London, p. 155 (1981).
10. A.G. Zdrak, *Elec. Chem. Tech. Russ.*, **60**, 120 (1992).
11. R.B. Goodrich and R.C. Evans, *J. Electrochem. Soc.*, **99**, 207 (1952).
12. T.B. Reddy, *Elec. Chem. Tech.*, **1**, 213 (1963).
13. J.L. Prentice, US Pat. 4,158,084 (June 12, 1979).

(*Received*: 21 March 2005; *Accepted*: 12 December 2005) AJC-4519