HYDROGEN STORAGE IN GLASS CAPILLARY ARRAYS FOR PORTABLE AND MOBILE SYSTEMS

Holtappels, K.[1], Beckmann-Kluge, M.[1], Gebauer, M.[1], Grüneberg, M.[1] and Eliezer, D.[2]
[1] BAM Federal Institute for Materials Research and Testing, Division II.1 "Gases, Gas Plants", Unter den Eichen 87, 12205 Berlin, Germany, Kai.Holtappels@BAM.de
[2] C.En Ltd., Sonnhaldenstraße 3, 8032 Zurich, Switzerland, DanE@cenh2go.com

ABSTRACT

A crucial problem of new hydrogen technologies is the lightweight and also safe storage of acceptable amounts of hydrogen for portable or mobile applications. A new and innovative technology based on capillary arrays has been developed. These systems ensure safe infusion, storage, and controlled release of hydrogen gas, although storage pressures up to 1200 bar are applied. This technology enables the storage of a significantly greater amount of hydrogen than other approaches. In storage tests with first capillary arrays a gravimetric storage capacity of about 33% and a volumetric capacity of 28% was determined at a comparative low pressure of *only* 400 bar. This is much more than the actual published storage capacities which are to find for other storage systems. This result already surpassed the US Department of Energy's 2010 target, and it is expected to meet the DOE's 2015 target in the near future.

Different safety aspects have been evaluated. On the one hand experiments with single capillaries or arrays of them have been carried out. The capillaries are made of quartz and other glasses. Especially quartz has a three times higher strength than steel. At the same time the density is about three times lower which means that much less material is necessary to reach the same pressure resistance. The pressure resistance of single capillaries has been determined in dependence of capillary materials and dimensions, wall thickness etc. in order to find out optimal parameters for the "final" capillaries. In these tests also the sudden release of hydrogen was tested in order to observe possible spontaneous ignitions. On the other hand a theoretical evaluation of explosion hazards was done. Different situations were analyzed e.g. release of hydrogen by diffusion or sudden rupture.

1.0 INTRODUCTION

A crucial problem of new hydrogen technologies is the lightweight and also safe storage of acceptable amounts of hydrogen for portable or mobile applications. A new and innovative technology based on capillary arrays has been developed for safe infusion, storage and controlled release of hydrogen gas [1]. Using single glass capillaries it is possible to store hydrogen as pressurized gas up to pressures of 1200 bar. The capillaries are molten at one end, the other one will be closed in a specialized storing procedure with an alloy. For the hydrogen release this end of capillaries has to be heated up to the melting point of the alloy. This principle is not only valid for single capillaries. It is also possible to bundled hundreds of them to capillary arrays. There is no limitation for the number of capillaries or their length and therefore every dimension of those arrays is possible. This enables one to produce such hydrogen storage systems for any kind of portable or mobile application.

In preliminary tests it was proven that the storage of great amounts of hydrogen is possible. A gravimetric storage capacity of about 33% and a volumetric capacity of 28% was determined at comparative low pressures of *only* 400 bar [2,3]. This is much more than the actual published storage capacities which are to find for other storage systems. This result already surpassed the US Department of Energy's 2010 target. It is expected to meet the DOE's 2015 target in the near future. First calculations showed that gravimetric storage capacities of about 50 % are possible at pressures of about 1000 bar.

The great advantage of glass capillaries especially those made from quartz is the higher strength compared to steel while having a lower density. Each capillary can be treated as a single pressure resistant vessel. Compared to steel vessels only a low wall thickness is necessary to reach the same pressures resistance. That means less material is needed and a lightweight storage system results.

Especially for mobile and portable applications the safety aspects are of great interest. No hazardous situations should occur due to unwanted release of hydrogen. Such release can be a result of diffusion processes or mechanical impacts. Furthermore strong heat impacts are critical for each storage system as it is possible for example in a fire. All these situations have been examined or theoretically evaluated for this new trendsetting storage system.

2.0 STORAGE PRINCIPLE

Single glass capillaries or already bundled capillaries (arrays) are installed in a larger pressure resistant vessel made from steel. The set-up is pressure resistant up to pressures of more than 1500 bar. The glass capillaries are closed by melting at one end, the other one will be closed with an alloy after adding hydrogen to the steel vessel. In a first step the set-up is evacuated. Afterwards hydrogen is filled into the vessel till the storage pressure is reached. This storage pressure is a flexible parameter and can be changed. Applying heat to one area of the set-up will melt the alloy which is closing the open end of the capillaries. In a specialized procedure the alloy will be slightly pressed into the capillaries so that after cooling the alloy respectively its solidification hydrogen is stored in the capillaries.

The hydrogen release is realized by carrying out the storage procedure vice versa. Heat is applied to the end of capillaries which is closed with the alloy. It will melt again and due to the high pressure in the capillaries hydrogen is released. Pressure control will be realized on the one hand by opening of specified areas of the arrays respectively by volume specification.

3.0 PRESSURE RESISTANCE

In the literature many properties for glasses are to find [4,5,6]. But no property is valid to describe sufficiently the resistance of glasses when there is a pressure inside of small structures. Therefore basic examinations have been carried out in order to determine the pressure resistance of round capillaries made from different types of glass. The outer respectively inner diameter and therefore the wall thickness are varied as well as the length of the capillaries (Table 1).

Table 1. Glass capillaries used for pressure resistance tests.

No.	Material	outer diameter [µm]	inner diameter [µm]	wall thickness [µm]	length [mm]
1	soda	400	300	50	100
2	soda	340	300	20	100
3	borosilicate	400	360	20	100
4	borosilicate	340	300	20	100
5	borosilicate	400	360	20	200
6	borosilicate	340	300	20	200
7	alumosilicate	400	300	50	100
8	alumosilicate	340	300	20	100
9	alumosilicate	400	300	50	200
10	alumosilicate	340	300	20	200
11	quartz	400	300	50	100
12	quartz	340	300	20	100
13	quartz	400	300	50	200
14	quartz	340	300	20	200

3.1 Experimental

The single capillaries have been glued into small 1/16`` stainless steel pipes in order to connect them to a set-up consisting mainly of a hydrogen supply, a compressor and a buffering vessel (Figure 1).

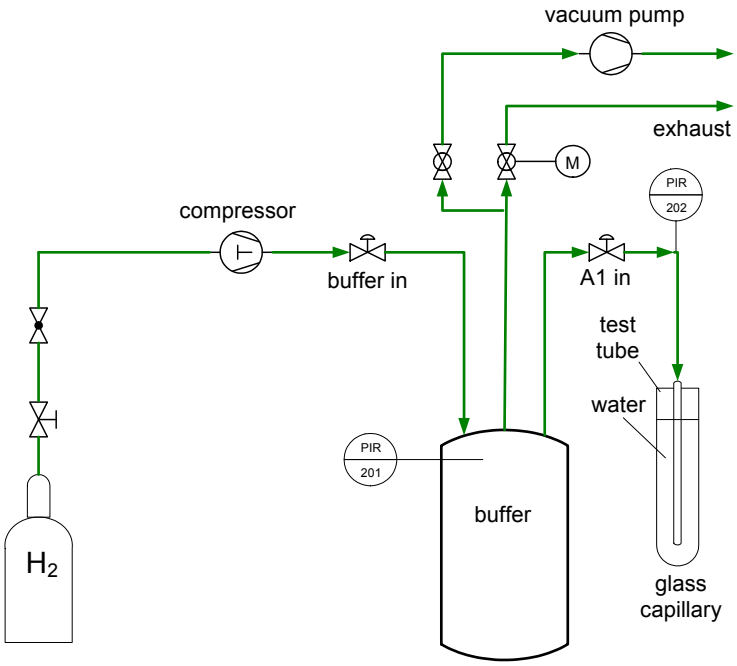

Figure 1. Schematically view of the set-up for the pressure resistance tests of glass capillaries

At first the set-up was evacuated. Afterwards hydrogen was filled to the capillary using a two stage compressor capable for pressures up to 1500 bar. In order to damp the hydrogen flow with each cylinder stroke of the compressor a buffering volume was installed between compressor and capillary. Two different filling speeds were realized by having different residence times during the compression of hydrogen (Figure 2). Close to the capillaries a pressure transducer was installed and the signal was recorded. Hydrogen was filled to the capillaries till they broke. The breakages have been recorded by high-speed video. Each capillary material and dimension was at least tested ten times.

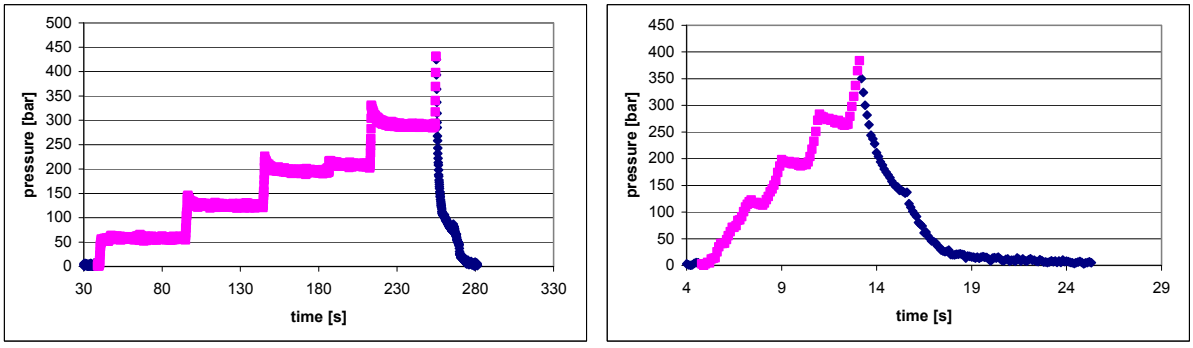

Figure 2. Pressure-time-history of the filling process of capillaries (left side: slow filling with intermediate times of residence; right side: fast filling without times of residence)

3.2 Results and Discussion

The burst pressures are summarized in Table 2. There are shown the average values of at least five pressure tests for each capillary. Furthermore the highest and the lowest burst pressure are mentioned.

Table 2. Burst pressures of the examined capillaries.

No.	Material	burst pressure in bar		
		average value	highest value	lowest value
1	soda 100 mm; 400x300	827	1147	250
2	soda 100 mm; 340x300	441	543	341
3	borosilicate 100 mm; 400x360	360	490	273
4	borosilicate 100 mm; 340x300	339	497	240
5	borosilicate 200 mm; 400x360	1002	1242	737
6	borosilicate 200 mm; 340x300	293	401	223
7	alumosilicate 100 mm; 400x300	484	591	351
8	alumosilicate 100 mm; 340x300	328	441	195
9	alumosilicate 200 mm; 400x300	460	535	421
10	alumosilicate 200 mm; 340x400	443	627	326
11	quartz 100 mm; 400x300	842	989	694
12	quartz 100 mm; 340x300	496	614	393
13	quartz 200 mm; 400x300	890	1091	394
14	quartz 200 mm; 340x300	382	562	146

No clear dependency was observed. Nor the material neither the wall thickness seems to influence the pressure resistance. The theoretically highest pressure resistance should be reached with quartz capillaries. But capillaries made from soda respectively borosilicate are able to withstand pressures more than 1000 bar. Moreover the highest average value (1002 bar) as well as the highest burst pressure (1242 bar) was determined for borosilicate capillaries with a wall thickness of 20 µm.

In Figure 3 the burst pressures for the capillaries with a length of 100 mm are shown. Plotted are the lowest burst pressures, the highest pressures and the average values calculated from all tests. For soda the highest burst pressure was detected, but also the lowest one. Nevertheless the average burst pressure is comparable to that one of the quartz glass capillary with the same dimensions.

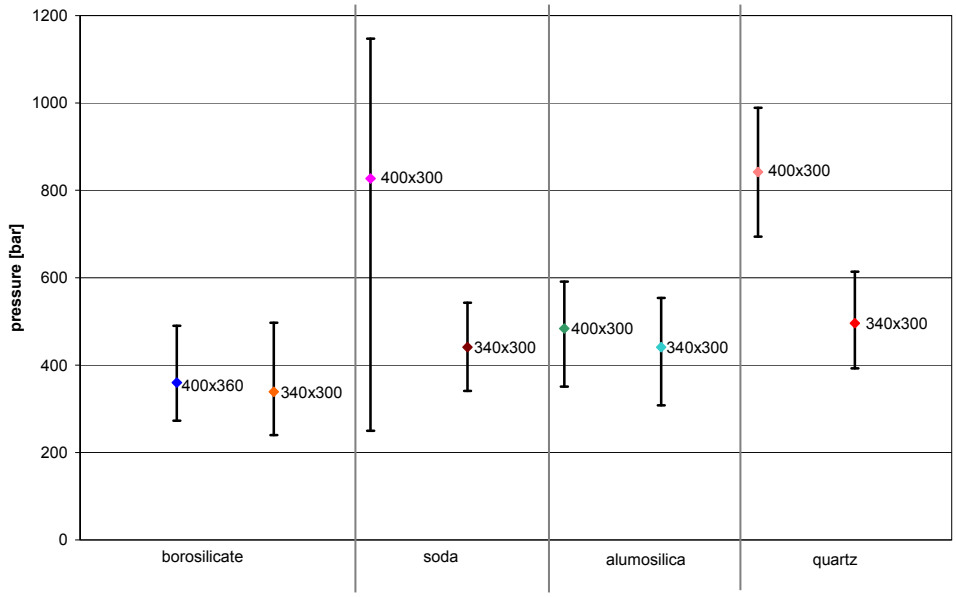

Figure 3. Burst pressures of single capillaries, length: 100 mm, various diameters and materials

There is a very critical effect influencing the pressure resistance of glass capillaries. Defects in the glass structures like bubbles, grooves or cracks flaws (shingles) will strongly increase stress peaks and therefore decrease the pressure resistance. Those defects have been observed for all examined capillaries (Figure 4).

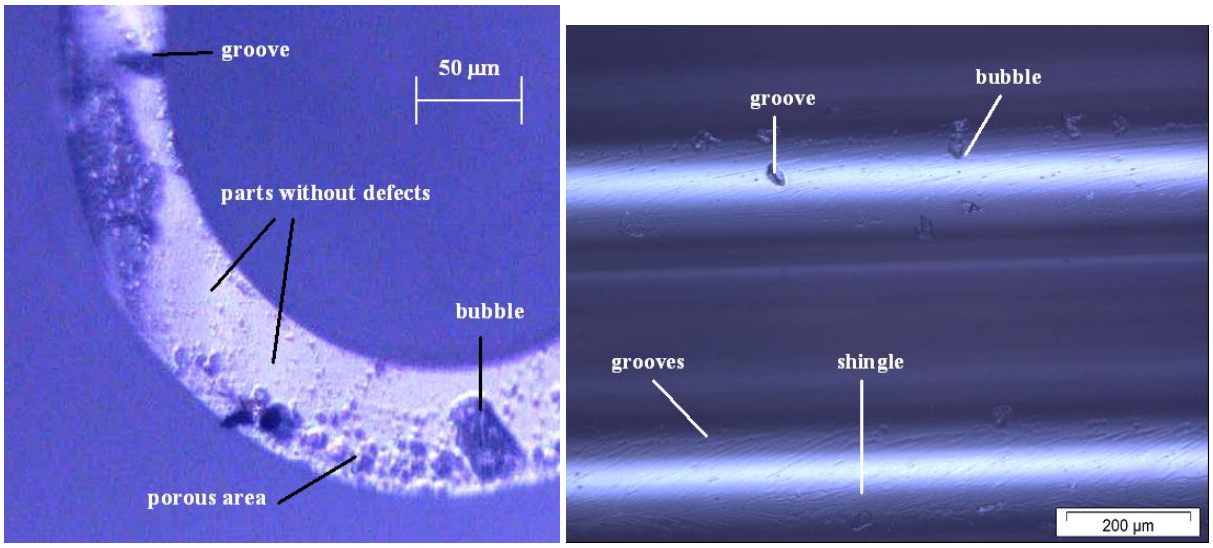

Figure 4. Microscope pictures from a soda capillary (left picture, view of cut end) and a quartz capillary (right picture, view of surface)

The effect of defects in the materials was also calculated by use of a numerical model. Two results are shown in Figure 5 where the stresses have been calculated for an inside pressure of 500 bar. If the capillary is without any defects the stress is homogeneously decreasing from the inside (198 N/mm^2) to the outside walls of the capillary (111 N/mm^2). In case of only one bubble in the wall a maximum stress peak close to the bubble was calculated with 557 N/mm^2. Recalculated strength from the burst pressure tests showed that the capillaries already broke at stresses of about 50 to 70 N/mm^2.

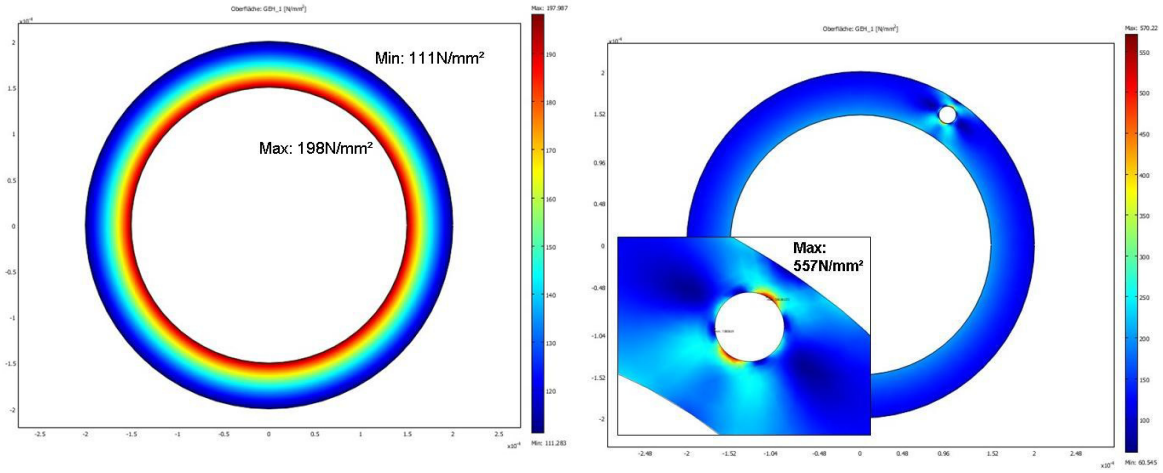

Figure 5. Calculated stresses in a quartz capillary, inside pressure 500 bar, left picture: capillary without defects, right picture: capillary with one bubble in the wall

4.0 HYDROGEN RELEASE

It has to be differentiated between a sudden and a slow hydrogen release. In this case slow release means hydrogen losses in the capillaries by diffusion. A sudden release always occurs when the structure itself was damaged. In the following the different scenarios are evaluated regarding the possible hazards arising due to the release of hydrogen.

4.1 Diffusion

An important fact is the diffusion of hydrogen through glass. This effect is slower than through steel. Nevertheless it has to be evaluated if hydrogen can be released in that amounts that the formation of an explosive atmosphere is possible. The diffusion process is strongly dependent on the temperature and the pressure inside the capillaries. In the literature is for example reported that no hydrogen diffusion was observed through various glasses at pressures of 1 bar and temperatures up to 640 °C [7]. Also no diffusion was observed at room temperature and 100 bar hydrogen for quartz glass [8].

For final storage systems no temperatures higher than 100 °C are to expect. The temperature can be of course partly higher at the end of capillaries which are closed by the alloy. Here temperatures of about 150 °C are possible during the filling process or the regular releases due to the heat apply. Nevertheless it is assumed that hydrogen diffusion at the most critical storage conditions (1000 bar, 100 °C) is very slow and can easily prevented by coatings at the surrounding of the capillary system. Even if hydrogen is released the amount should be too small to build e.g. explosive atmospheres.

4.2 Rupture

In principle each capillary is a pressure resistant vessel, able to withstand pressures higher than at last the storage pressures (factor 1.2 is aspired). Nevertheless glasses are amorphous materials which can easily break in case of impacts. In this case the complete amount of hydrogen will be released at once. The rupture of one single capillary is not that critical. The released amount of hydrogen is too small to form explosive atmospheres. Critical might become situations in which a major number of capillaries are broken and the complete stored hydrogen is released.

In the literature the spontaneous ignition of hydrogen is reported when it is released from high pressure to atmospheric pressure [9]. During the pressure resistance tests the capillaries were observed by high-speed video in order to see the rupture of the capillaries in details on the one hand. On the other hand possible spontaneous ignitions should also be visible. In all tests where the different capillaries burst at different pressures no ignitions were observed. In Figure 6 a sequence of a high-

speed video is shown when a quartz capillary burst at a pressure of 850 bar. It was recorded with 17.900 frames per second. In only three successive pictures the burst can be seen in detail. At first the capillary broke at one half, afterwards the other half was cracked.

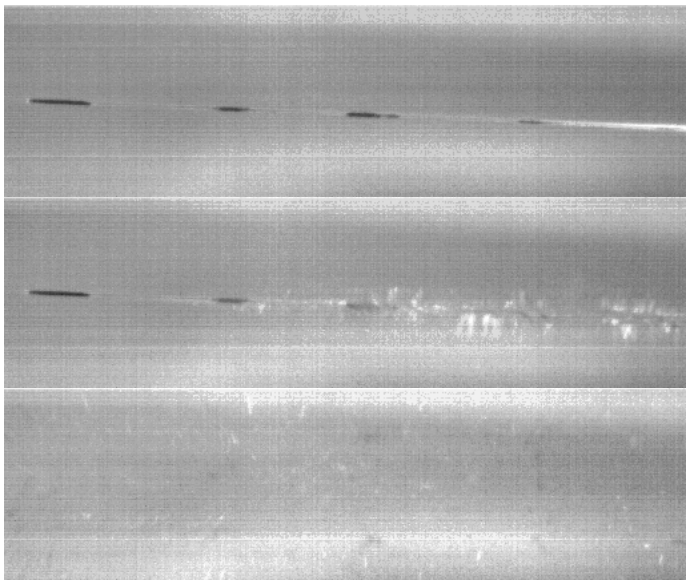

Figure 6. Burst of a quartz capillary (400 μm x 300μm) at a pressure of 850 bar

5.0 CONCLUSIONS AND FUTURE PROSPECTS

The hydrogen storage in glass capillaries is innovative and of trendsetting nature. In the near future it might be possible to use such lightweight systems in broad fields of energy related applications like electronics or vehicles.

The safety of such systems is of course very important. At this time basic tests and safety evaluations showed that these glass structures might be safer than those which only consist of one single vessel. If a sudden release occurs in case of a one vessel system the large amount of hydrogen will lead to critical situations. In case of the multi-capillary system the release is strongly dependent on the kind of impact. The advantage of such capillary array systems is the bundling of many single capillaries, each of them can be seen as single pressure vessel. If one “vessel” is damaged no hazardous situation is caused due to the release of only small amounts of hydrogen. No overpressure appears or even spontaneous ignitions as they were sometimes observed when hydrogen was suddenly released to the atmosphere. Furthermore no explosive atmospheres are formed because the absolute amount of hydrogen was too small.

To further optimize the storage capacities over a long time, coatings for the capillaries will be developed in order to minimize hydrogen losses by diffusion. Subsequently the optimized single capillaries were bundled to arrays consisting of different numbers of capillaries. These arrays were used for many safety tests. In most of them the behavior of the arrays was determined when they were mechanically damaged or heated externally by fire. In case of ruptures or damages the sudden release was noticed.

Many tests were actually carried out with single capillaries. The “numbering up” or bundling has to be examined, too. There are still open questions, e.g. the strength of the capillaries in dependence of wall thickness, long term storage pressures, mechanical impact, and fire treatment of capillary arrays.

REFERENCES

1. http://www.cenh2go.com/
2. Holtappels, K., Storage of Hydrogen in Capillary Arrays, BAM Federal Institute for Materials Research and Testing No. Vh. 2516 – Progress 09/2008
3. Holtappels, K., Storage of Hydrogen in Capillary Arrays, BAM Federal Institute for Materials Research and Testing No. Vh. 2516 – Review 2008
4. Varshneya, A. K., Fundamentals of Inorganic Glasses, Academic Press, New York 1994 p. 409
5. Zarzycki, J., Glasses amd the vitreous state, Cambridge University Press, Cambridge 1982
6. Bansal, N. P., Dorhemus, R. H., Handbook of glass properties, Academic press 1986
7. Williams, G. A. and Ferguson, J. B., The Diffusion of Helium and Hydrogen through Silica Glass and other Glasses, J. Am. Chem. Soc., 1922, 44 (10), pages 2160-2167
8. Elsey, H. M.; The Diffusion of Helium and Hydrogen through Quartz Glass at Room Temperature, J. Am. Chem. Soc., 1926, 48 (6), pages 1600-1601
9. Astbury G. R. and Hawksworth, S. J., Spontaneous ignition of hydrogen leaks: A review of postulated mechanisms, International Journal of Hydrogen Energy, Volume 32, Issue 13, September 2007, Pages 2178-2185