

Study of The Chemical Durability and Hazardous Ionic Leaching of(Soda-Lime) Glass

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Abstract

Huge amounts of glass materials being applied in medical, pharmaceutical and chemical aqueous solutions; this requires the study of chemical stability of glass at the exposed surfaces with these solutions where the leaching takes place.

The leaching of the glass ions will transport these ions to the solutions stored in the glass containers; leading to changes in the chemical composition in the order of part per million that causes hazardous effect with time.

The present work investigates the leaching chemical properties of the soda-lime Iraqi glass containers. The effect of the pH of contact solution and annealing of glass on leaching rates is studied. Ionic leaching shows lower rate with PH of the solutions at the 'safe zone': ($6 > \text{PH} > 8.5$). Annealing increases the leaching rates and reduces of the chemical durability of glass. Increasing annealing time led to further increase the leaching rate. In addition, the increase in the exposed surface area also increases leaching rates.

Keywords: chemical durability, ionic leaching, Soda-Lime- glass, annealing

دراسة المتانة الكيماوية وضرر النضوح الأيوني لزجاج الصودا - لايم الخلاصة

أن المدى الواسع لتطبيقات المواد الزجاجية في أساليب حفظ المحاليل الطبية والصيدلانية و الكيماوية يتطلب دراسة مدى الثباتية الكيماوية لايونات الشبيكة الزجاجية المكونة لهذا النوع من الزجاج وذلك من خلال التماس الحاصل بين المحاليل الكيماوية والسطوح الزجاجية المعرضة لمثل هذه المحاليل محدثة نضحا أيونيا . أن هذا النضح سيؤدي إلى انتقال تلك الايونات إلى المحاليل المخزونة مما يغير في التركيب الكيماوي لتلك المحاليل ولو بنسبة جزء من المليون , ولكن تأثيرها سيكون مؤثرا بصورة سلبية بمرور الزمن .

يتعرض العمل الحالي الى تشخيص الخواص الكيماوية لزجاج الاوانسي العراقية المصنوع من (الصودا-لايم) حيث تم دراسة تصرف النضح الايوني للزجاج وتأثير الدالة الحامضية والقاعدية للمحلول المسبب للنضح , وأثر المعاملة الحرارية للزجاج على معدلات النضح الايوني لايونات لشبيكة الزجاجية وتبين من خلال النتائج إن النضح الايوني يكون في أقل مدياته عند قيم الدالة الحامضية التي تبعد عن المنطقة الامنة ما بين (6-8.5) . وقد تغير معدل النضح وأزداد بشكل كبير لمديات الدالة الحامضية التي هي أقل من 6 أو القاعدية التي هي أعلى من 8.5 , وكذلك أدت المعاملة الحرارية (التلدين) الى زيادة معدل النضح وقللت من المتانة الكيماوية للزجاج , وأن الزيادة في زمن المعاملة الحرارية قد زاد من معدلات النضح كما أن الزيادة في المساحة السطحية المعرضة قد أدت الى زيادة معدل النضح .

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Introduction

Pure silica SiO_2 melts at about 2000°C . Glass can be made from bare silica for special purposes. Additives like Na_2CO_3 lower the silica melting point and bring it to 1000°C . In addition, large amounts of additives make the glass water soluble. The lime (CaO) which is produced from limestone (CaCO_3), magnesia (MgO) and alumina (Al_2O_3) may be added to enhance chemical durability. The formulated soda-lime glass should be composed of 70-72 wt% which represents 90% of glasses industry^[1]. Glasses that do not include silica as a major constituent may have physico-chemical properties that are useful for special application like fiber optics and other dedicated technical applications^[2]. The corrosion of glass surface by aqueous solutions was associated with the term "chemical durability" which was conventionally used to express the resistance of glass against attack by aqueous solutions and atmospheric means. There is no explicit measure for the chemical durability; therefore, the results are usually compared after subjecting glasses to the same experimental condition. But, the nature of the experiments usually determines the relative order. These experiments are usually interferometry and weight loss measurement on the attacked glass as well alkali metric titration, PH and electrical conductivity measurements on the solutions. A complete analysis of the leached ions in the solutions and the attacked glass surface provides phenomenological information for the various factors involved in the corrosion of glass^[3].

Experimental part:

The soda-lime glass that represent the Iraqi glass containers are subjected to the ionic leaching. Table (1) shows the chemical composition of that glass.

The glass samples were prepared by cutting to square shaped pieces of (50×50×4mm). These samples are weighted by four digit sensitive balance. Then alkali and acidic aqueous solutions are prepared given PH (1, 3, 4, 6, 9, 10.5, 11.5 and 12.5). The samples were immersed in the aqueous solutions. The ratio of the volume aqueous solution (ml) to sample surface area (mm^2) is 10 simulating Petit and Dran experiment^[4]. Some of these samples were annealed after immersion at 700°C for different periods of time (1, 2, 3 and 4 hrs).

The immersed samples were withdrawn from the solutions after 30 days for test. Then, leaching solution samples of 10ml are chemically analyzed by atomic absorption to determine the weight of the leached ions for each glass. Leaching rates were calculated by the following equation^[3]:

$$\text{L.R.} = a_0/A_0 \times w/S \times T \quad [\text{g}/\text{cm}^2.\text{day}]$$

L.R.: leaching rate.

a_0 : Leachant ion weight (in aqueous solution).

A_0 : Initial weight of ion in the glass sample.

W: Initial weight of glass sample [g].

S: The surface area of sample [cm^2].

T: immersion time [day].

Results and discussion:

The results of ionic leaching rates are shown in the figure (1). The ionic leaching rate at pH=1 are relatively high for the three leached

ions (Na, Al and Ca) compared with the results at pH=3. When the acidity is further decrease to PH=4, 6, the leaching rates show lower values. This behavior is mostly clear for the calcium ions compared with the other two ions. The calcium has its lower leaching rate at PH=9 and then, continue increasing the leaching rates as the PH increases. Generally, increasing the PH of alkali aqueous solutions increases ionic leaching rates. These results agree with that of Petit and Dran experiment ^[4].

At low pH, the leaching was also obvious but shows lower values than that of high PH. At pH=4-8, the lower leaching rates is observed. This range is named the "safe zone" and suggested for pharmaceutical applications.

The results for the heat treated glass samples are shown in figure 2. The ionic leaching rate increases with heat treated samples compared with that non heat treated. Generally, the heat treatment shrinks the safe zone. This can be explained by the formation of grain boundaries with a low atomic backing which readily react with the leachant. This result is in agreement with the work of Elliot ^[5].

The results shown in figure (5) illustrate the effect of heat treatment time on ionic leaching rate. The increase of heat treatment time increases ionic leaching rate, this behavior is general for the three selected ions. These results explain that the increase in heat treatment time increases the crystallization and grain boundary area, accordingly, the leaching rate.

The results shows that the increase in surface area of glass samples increases ionic leaching the rates (figure 6). Normally, this is expected due to that the increased contact area enhance the number of ions that are subjected for reaction.

Conclusions:

1. The PH of solution shows major effect on chemical durability of glass, and the safe zone of PH is (6-8.5) for the Iraqi soda lime glass.
2. Leaching rate increases with heat treatment time and the exposed area of glass.

References:

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Table(1) Chemical analysis of the Iraqi soda lime glass

Oxides	wt%	Oxides	wt%
SiO ₂	72.6	MgO	0.57
AL ₂ O ₃	1.1	Na ₂ O	15.6
Fe ₂ O ₃	0.11	SO ₃	0.07
CaO	9.14		

Table (2) Leaching rate values of Sodium, Aluminum and Calcium for non heat treated glass

PH	L.R. (g/cm ² . Day)		
	Na	AL	Ca
1.	9.	1.	7.
3.	6.6	3.	2.3
4.	6.	4.	0.84
6.	5.	6.	0.84
9.	8.	9.	0.91
10.5	55.	10.5	1.67
11.5	600.	11.5	3.
12.5	550.	12.5	9.

Table (3) Leaching rate values of Sodium, Aluminum and Calcium for heat treated glass

PH	L.R (g/cm ² . Day)		
	Na	AL	Ca
1.	100	200.	55
3.	55	150.	6.6
4.	9	100.	5.
6.	7	83.3	1.67
9.	45	78.	1.
10.5	550	16.7	4.
11.5	8700	360.	6.6
12.5	8900	1000.	10.

Table (4) Leaching rates values versus heat treatment time for glass at (700°C)

Time of heat treatment (hr)	L.R. (g/cm ² . Day)		
	Na	AL	Ca
0	77	180	4000
1	17.5	350	6000
2	9	400	7500
3	85	1250	8500
4	85	9000	25000

Table (5) Leaching rate values versus sample surface area (PH =12.5)

Surface area (cm ²)	L.R. (g/cm ² . Day)		
	Na	AL	Ca
0	0	0	0
10	0.75	1	2
25	8	35	300
30	30	60	850
35	75	200	4000

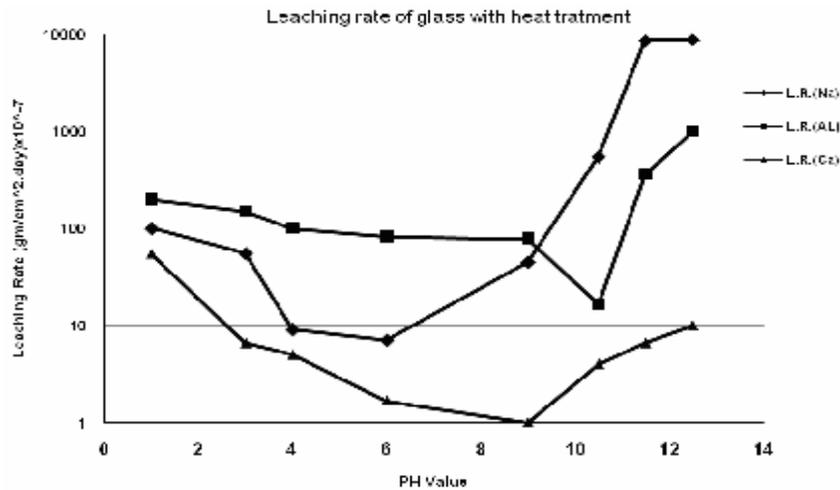


Figure (1) Leaching rate versus PH value of glass without heat treatment.

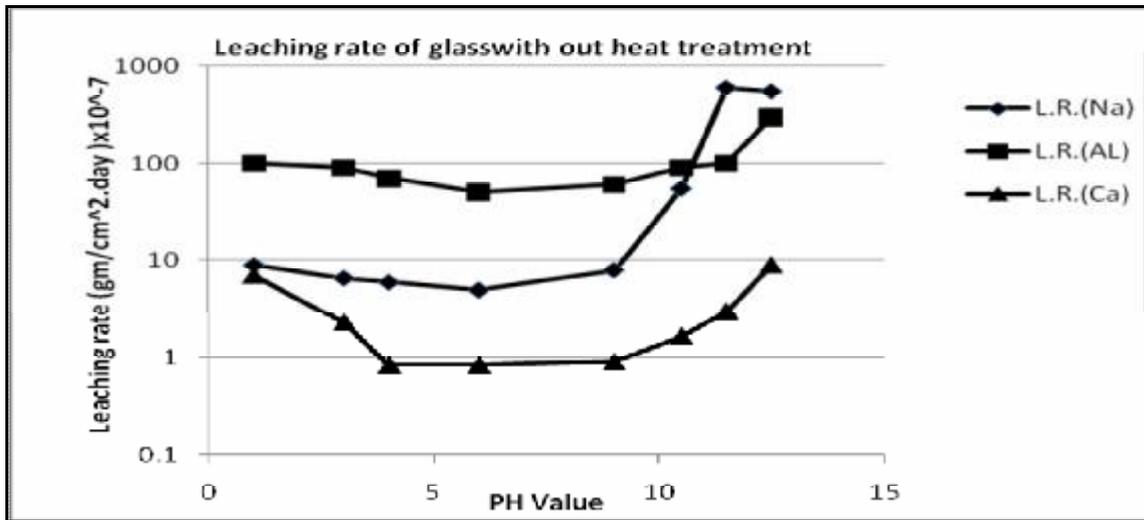


Figure (2) Leaching rate versus PH value of glass element with heat treatment.

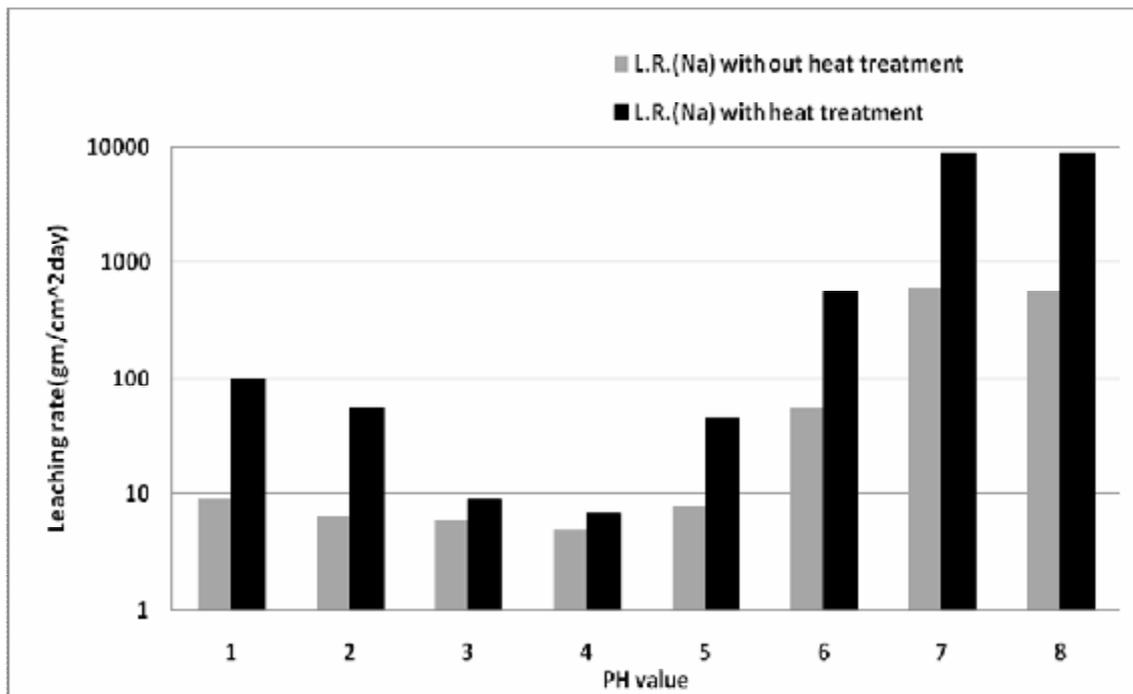


Figure (3)-a: Leaching rate versus PH value for (Na) element

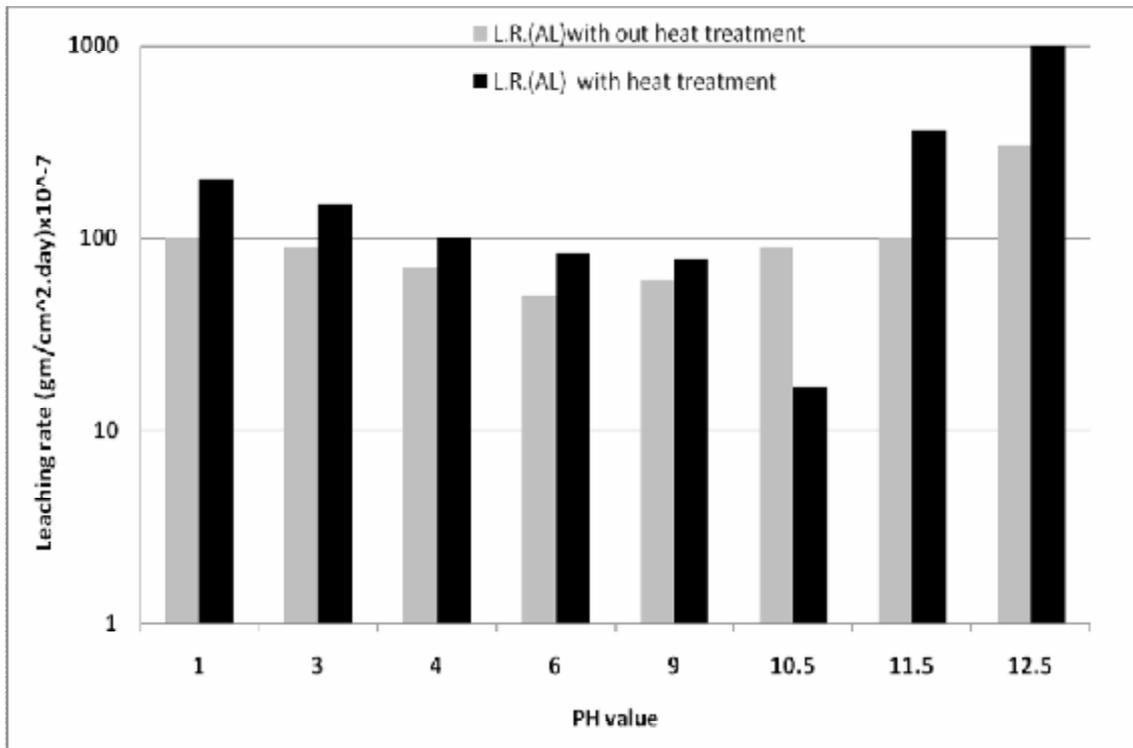


Figure (3)-b: Leaching rate versus PH value for (AL) element

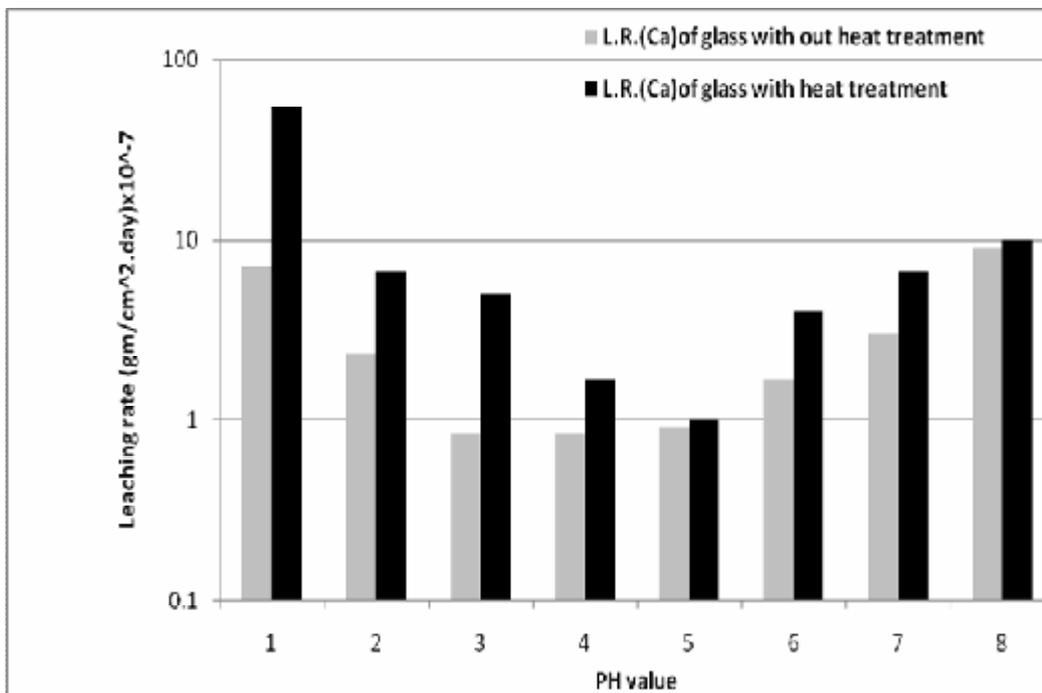


Figure (3)-c: Leaching rate versus PH value of (Ca) element

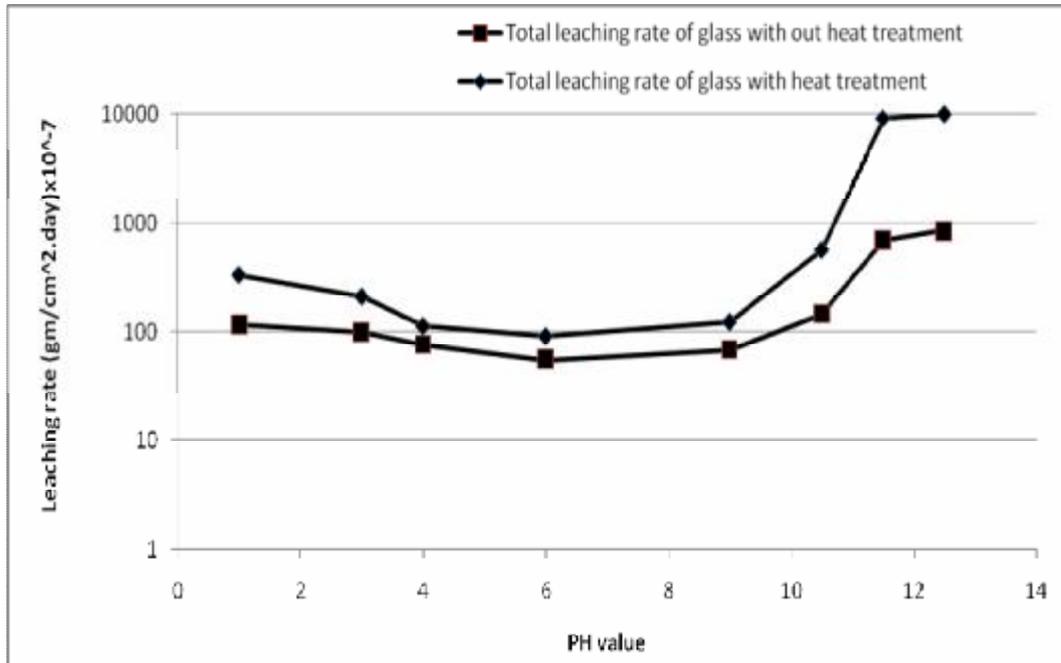


Figure (4): Total leaching rate of glass versus PH values.

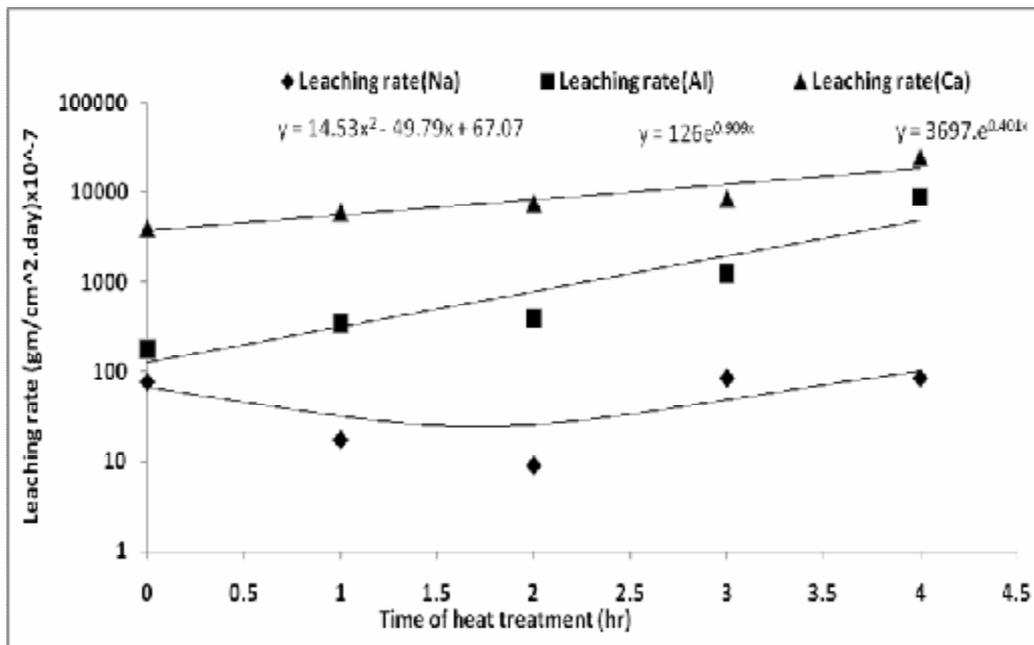


Figure (5): Leaching rate versus time of heat treatment at PH =12.5.

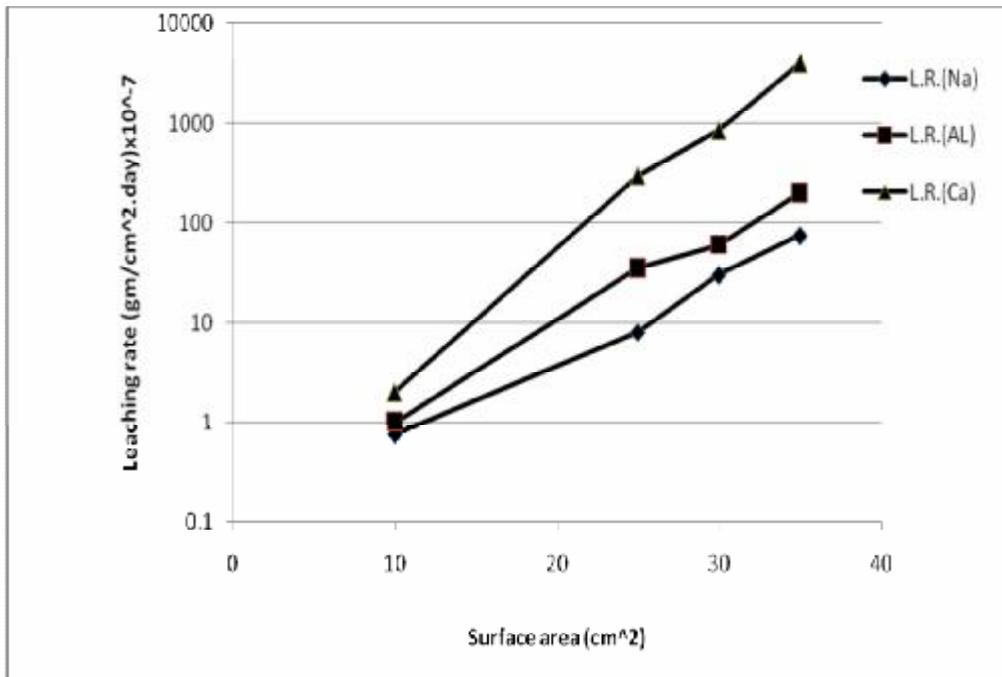


Figure (6): Leaching rate versus surface area of glass samples at PH =12.5.