Chemical and mechanical tests on the SiO$_2$-ZnO materials for protective coatings of industrial use

A M Mocioiu$^1$, D I Băilă$^2$* and O C Mocioiu$^3$*

$^1$National R&D Institute for Non-ferrous and Rare Metals, 102 Biruinţei Blvd, Pantelimon, Ilfov 077145, Romania
$^2$University Politehnica of Bucharest, Blv. Splaiul Independentei, no. 313, sector 6, cod 060042, Bucharest, Romania
$^3$Ilie Murgulescu Institute of Physical Chemistry of Romanian Academy, 202 Splaiul Independenţei, Bucharest, Romania

E-mails: baila_d@yahoo.com, oana.mocioiu@yahoo.com

Abstract. Many industrial processes, such as chemical process and pharmaceuticals, use aggressive acidic and caustic solution which may result in an early failure of the components of plant. The various corrosion processes in harsh environments could be uniform corrosion, localized corrosion, galvanic corrosion, etc. In order to extend the life of components, a proper material selection is necessary. This direction is intended to address the behaviour of materials due to exposure in harsh environments. The main objective is to develop new vitreous coatings for different kind of materials as metals or glasses in order to protect them against acid attack. SiO$_2$-ZnO materials were prepared by chemical route in order to be used as protective coatings. The SiO$_2$-ZnO materials were investigated by infrared spectroscopy and differential thermal analysis in order to determine their structure and thermal characteristics. SEM and EDS measurements were performed to investigate their structure and morphology. The chemical resistance tests in acid media (HCl and HF) were followed based on STAS and ISO standards and the extraction solutions were tested by ICP-MS in order to identify elements lost during tests. Mechanical tests were performed.

1. Introduction

Many industrial processes, such as chemical process and pharmaceuticals, use aggressive acidic and caustic solution which may result in an early failure of the components of plant [1,2].

In the industry are used reactors made from various materials as steel, glass, cement, titanium, etc. [3,4,5]. Each of them is used according with reactions that are performed inside.

Glass reactors are transparent equipment that is used in the production of chemicals, polymers, and pharmaceuticals. They comprise strong glass walls that shield the interior contents from any exposure to or contact with the outside world. In doing so, they facilitate the reactions of substances. Glass reactors are mainly used for synthetic reaction, distillation and concentration of different types of materials. In the pharma industry are used glass reactors in order to prevent the metal contamination for high pure drugs and biological materials.

There are few types of glass reactors used in the Pharma Industry as:
- The batch glass reactor is mainly used for those small-scale applications. Though simple, this kind of reactor has the ability to accommodate many kinds of gears at a time. Indeed, it will receive all the materials until such a time that the capacity is packed to the brim [3].

- The continuous stirred-tank reactor model where one or more liquid reagents are introduced into the tank segment. This mixture is subsequently stirred using an impeller to mix the reagents fully and uniformly. In this way, the reagents produce great outcomes indeed. This kind of reactor is larger than the batch glass reactor. It finds applicability in those areas that demand industrial-size applications; that include the brewing, pulping, and handling of various biological materials [3].

- The continuous tubular reactor accepts one or more fluid reagents from a side to side tube or pipe. In this reactor, the chemical reactions will transpire simultaneously with the movements of the reagents from the tubes into the tubular reactor. As these reagents mix, the rates vary significantly in such a way as to generate a gradient that is further characterized by added admiration. This reactor is mainly useful for mass production where many ingredients have to be mixed and handled at a time [3].

- Catalytic Cracker. Catalytic cracking is a chemical process that entails the extensive use of carbon ions. The cracker is mainly used to convert the high molecular weights of the hydrocarbons into more valuable small molecular hydrocarbons [3].

The various corrosion processes in acid environments could be uniform corrosion or localized corrosion. In the case of hydrochloric acid corrosion on reactors it is uniform corrosion and it can cause contamination of products. Glass reactors can be used in industries were small quantities of contaminants have influence on the properties of product as pharmaceutics.

In order to extend the life of components of reactors and industrial plant, a proper selection of the material is necessary. Other method used in industry is coating the inside part of the reactor with an anticorrosive material. The chemical stability of the glasses can be improved by depositing protective layers of metal oxides (SnO₂, TiO₂, CuO, ZnO) or films of organic compounds [6-10].

The main objective of this paper is to develop new vitreous coating for glass reactors in order to protect them against acid attack. The SiO₂-ZnO composition was choosing in order to maintain the vitreous character of protective film and also due to well-known antibacterial role of zinc.

The literature data report obtaining of glasses synthesized by classical route of melt-quenching in the SiO₂-ZnO system in compositional domain between 0-35 mol % ZnO [11, 12]. The classical route imply high melting temperature (>1400°C) and the deposition on other glass cannot be performed.

In order to obtain SiO₂-ZnO vitreous films on glass substrate, a precursor solution was prepared by sol-gel and dip-coating method was used for deposition.

2. Experimental parts
Coatings with 7% ZnO and 93% SiO₂ were obtained by deposition of thin films by dip-coating of precursor solutions obtained by sol-gel method. The method to prepare similar precursor solution was presented in a previous paper [12]. Precursor solution with molar ratio: C₃H₇OH: TEOS: H₂O: HCl = 10: 1: 3: 0.03 was prepared. Doping with 7% zinc oxide was achieved by adding zinc acetate dehydrate at precursor solution and mixing for 2 hours. Thin films were obtained by dip-coating of solution on glass substrates and thermally treated at 500°C.

STA/TG measurement on gel was made with a Setsys Setaram equipment with 10 degrees/minute between 20-900°C.

The chemical resistance tests in acid media (HCl 37% and HF 35%) were performed based on STAS 598/3-76; STAS 2413-87 and ISO 1776:1985 [13, 14, 15]. In order to simulate a long period of contact between acid media and reactor wall, the samples were boiled at 100°C in acid time to 2 hours. The extraction solutions were tested by ICP-MS in order to identify elements lost during tests.

Morphology and composition of samples before and after acid attack were studied with a scanning electron microscope (SEM) Quanta 250, produced by FEI Company, incorporated with Energy Dispersive X-Ray Spectrometer, produced by EDAX, consisting of ELEMENT Silicon Drift Detector Fixed, Element EDS Analysis Software Suite.
MHT-10 Microhardness tester, produced by Anton Paar, with Vickers indenter was used for mechanical properties. The tester was bonded with electronic microscope with polarized light Carl Zeiss Microimaging Gmbh, equipped with a digital camera for photo acquisitions and soft AxioVision Release 4.8.1 for image processing.

3. Results
The 93% SiO$_2$-7% ZnO gel was investigated by STA/TG and FT-IR in order to determine their thermal behaviour and structure. Gel obtained after drying of precursor solution at room temperature was studied. Figure 1 present the FTIR spectrum of 93% SiO$_2$-7% ZnO gel. Figure 2 show the STA/TG curves of 93% SiO$_2$-7% ZnO gel.

In order to record FTIR spectrum, the sol with composition 93% SiO$_2$-7% ZnO was dried at room temperature and 1 mg powder was mixed in a pellet with 200 mg KBr. The recorded spectrum shown the bands characteristic to Si-O vibrations similar with those reported in literature [16-21]. Main bands at 1223 cm$^{-1}$, 1088 cm$^{-1}$, 795 cm$^{-1}$ and 463 cm$^{-1}$, are assigned to Si-O-Si bonds in network, chains and band at 950 cm$^{-1}$ is characteristic to isolated [SiO$_4$] tetrahedra; while the small band at 555 cm$^{-1}$ can be assigned to vibration of the Si-O-Zn bonds. The FTIR spectrum show shape of vitreous material due to wide bands. The band position of vibration of the bonds between Si-O and Zn-O appear in the spectrum but they cannot be assigned to a crystalline form. So, the film on the glass substrate has also vitreous structure. The bands at 3478 cm$^{-1}$ and 1643 cm$^{-1}$ are assigned to vibration of the O-H in the absorbed water.

![Figure 1. FTIR spectrum of 93% SiO$_2$-7% ZnO gel](image1.png)

![Figure 2. STA/ TG curves of 93% SiO$_2$-7% ZnO gel](image2.png)
STA curve shown main endothermal effect between 32°C and 126°C corresponding to elimination of water and alcohol from obtained sol. Mass loss was of 12 %. As can be seen in the figure after 500°C the loss mass is zero. Thermal treatment at this temperature was established because the elimination of residual solvents was complete and glass substrate is not modified by treatment temperature.

The film deposited on glass substrate from precursor solution and thermally treated at 500°C was investigated from structural and morphological point of view using SEM / EDAX methods.

Figure 3 show SEM image of the film with morphology characteristic for glasses and EDAX of 93% SiO₂-7% ZnO film. The material have a uniform and homogeneous morphology. Identified position of Si and Zn in EDAX of the film are similar with literature data [8, 14].

![Figure 3. SEM/EDAX of SiO₂-ZnO film](image.png)

The chemical resistance tests in acid media (HCl and HF) were followed based on STAS 598/3-76; STAS 2413-87 and ISO 1776:1985 [9, 10, 11] and the extraction solutions were tested by ICP-MS in order to identify elements lost during tests.

Figure 4 show SEM images of SiO₂-ZnO film after acid attack with HCl and HF. The morphology of the films surfaces after corrosion tests was studied by scanning electron microscopy. Figure 4 displays both morphologies. In case of HCl attack a network of mottled material, as usually happens in hydrated silica layers was evidenced while in case of HF attack can be seen a change of the morphology. In case of glasses are well known 5 corrosion mechanism. In case of acid attack of the film two mechanism can be observed. In case of HCl attack the formation of a silica-rich film without destruction of the silicate network due to the strength of the acid is observed. In case of HF attack the concentration of ions in solution is high enough and the loss of silica atoms from glass network cannot be prevent until the equilibrium of reaction.

By exposing hot glass surfaces to the action of volatile compounds with flour, an increase in chemical resistance occurs without forming visible reaction products on the surface thus treated.

Chemical resistance is increased due to the replacement of O²⁻ and OH⁻ ions on the surface glass, by F⁻ ions. Fluor ions penetrate deep into the silico-calco-sodium glasses and not are abundant on the surface of the glass [6]. Improving chemical and mechanical strength can be achieved by treatment with fluorine-based compounds [7].

Although random wet etching with a hydrogen-fluoride (HF)-chemical solution is a simple and inexpensive method, a non-uniformly-etched surface is produced due to the remains of the insoluble product present in the chemical solution [22,23]. The HF-solution-based etching also leads to an increased haze value, which has an adverse effect on the improvement of the transmittance. Park [22] reported a geometrical hemisphere-array structure developed with a textured-glass substrate using the HF-H₂SO₄ wet-etching method. The height profiles glasses corroded with solutions of 10%, 25% and 35% concentration correspond to texture etched sizes. The morphology was modified in order to increase optical properties and chemical resistance of the glasses.
ICP-MS measurements after corrosion tests show extraction of 20 ppb Zn from film after HCl attack and 40 ppm zinc and 20 ppm Si from film after HF attack. In the case of HCl attack, zinc ions are extracted at the level of ppb and silica extraction is not observed. This result is in agreement with previous observation in SEM image and confirm formation of silica-rich film without destruction of the silicate network. In case of HF attack, higher quantities of both ions Zn and Si are extracted and the result confirm the glass network destruction observed in SEM image. The attack of HF was much higher than attack of HCl. In case of HCl, the equilibrium is obtained and the silica-rich film acts as a barrier and corrosion is stopped. In case of HF, the destruction of silica network will continue and new atomic layers will dissolve in solution, but if the time set until the equilibrium of the corrosion reaction is reached, then the changed morphology will probably have a higher chemical resistance.

![Figure 4](image1.png)  
**Figure 4.** SEM images of SiO$_2$-ZnO film after acid attack: a) HCl and b) HF

Microhardness tests were performed on the studied film deposited by dip-coating on glass. Figure 5 show the indentation prints were small. When the crack appeared in the corner of the indentation prints they propagated in the film and not to interface. The force used in determination was 2N, time to 2s, slope 0.6N/s.

The measurements were repeated three times and the results were between 765 and 780.

![Figure 5](image2.png)  
**Figure 5.** Micro hardness prints on SiO$_2$-ZnO film deposited on glass
4. Conclusions
The chemical resistance of 93% SiO$_2$ -7% ZnO film deposited on glass in acid media (HCl 37% and HF 35%) was different.

The way in which the surface of the film deposited on the glass reacts to the attack of acids is greatly influenced by the strength of the acid used.

The mechanical resistance HV was between 765 and 780 and it is a good resistance for glasses.

The studied film can be used as protective film for glass reactors that work in acid media as some polymer synthesis.

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