

Their presence can do damages in the environment that is why their amount is regulated by law. Currently, establishments produce paints and varnishes set for each product safety data sheet preparation which is showing its compliance with the applicable legal standards.

Waste paper has been divided according to the color and type of paper. They separated the following fractions: yellow, red, purple, blue, green and black and thick paper, cardboard and drawing paper. The materials were cut into small pieces. Then the samples were flooded with distilled water in the ratio 1: 2 (one part of waste to two parts of water) and subjected to fiberization. After two weeks of storage water extracts were prepared by manual separation of the eluate and allowed to stand in sealed jars for one week.

To determine the content of individual elements was used the photometer, also the pH was determined. The concentrations of the following metals: chromium, cadmium, zinc and nickel were tested. The results are presented in table (Table 1. Results of measurements). Several values is above the maximum values specified in the Regulation of the Minister of Environment of 18 November 2014. On the conditions to be met during placing waste in water or ground and on substances particularly harmful to the aquatic environment (Dz. U. 2014 pos. 1800).

**Table 1. Results of measurements**

Waste group (color / type)	Element [mg/l]				pH	p
	Chro-	Cadmiu	Zinc	Nickel		
Green	0,051	0,459	<0,500	<0,02		6
Red	0,050	0,237	0,265	<0,02		5
Black	0,059	0,464	0,039	<0,02		6
Purple	0,172	0,553	<0,500	0,029		6
Blue	0,214	0,359	0,014	0,835		6
Yellow	0,016	0,489	0,132	<0,02		6
Thick paper	0,027	0,322	0,025	1,318		5
Drawing paper	0,018	0,297	<0,010	<0,02		5
Cardboard	0,059	0,579	<0,010	0,132		6
<b>Limit value Dz.U. 2014 pos. 1800</b>	0,1	0,4	2	0,5		6
						,5-9

The test results show that in all the samples the pH values are too low. The limit value for cadmium is exceeded for the five samples. Aqueous extracts of the violet and blue paper showed exceeded for three pollutants (chromium, cadmium and nickel). The value of the concentration of nickel is the most exceeded in eluate from thick paper - almost three times the limit value.

Taking into account results obtained in test it is difficult to provide a trend. Noteworthy are samples of blue and purple paper. Inks of these colors contain the largest amount of hazardous ingredients. In summary, the test shows that the amount of the metal varies depending on the type of paper and even its color. These values are not harmful to health, but keep in mind that the more, for example on a wild landfills have a negative impact on the environment.

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## **POROUS SILICON (CARBO) NITRIDE LAYER STRUCTURES FOR SEPARATION APPLICATIONS**

### **Abstract**

Layered structures consisting of silicon (carbo)nitride were prepared for a use in separation applications. The focus was set on finding a processing routine for these structures using a dip coating procedure, which becomes possible through utilization of preceramic polymers. Two types of supports were prepared to provide different substrates for the deposition of the following layers, one being a polymer derived ceramic (SiCN) involving the use of sacrificial fillers, the other conventionally prepared via slip casting ( $\text{Si}_3\text{N}_4$ ). The second layer was deposited via dip coating using a combination of preceramic polymer and silicon nitride particulates, forming a composite layer after pyrolysis of the polymer. The final layer, the selective layer, is responsible for the separation and was prepared via dip coating of the preceramic polymer. The resulting structure possesses graded multiscalar porosity, providing sufficient selectivity and permeability in prospective applications such as gas or liquid separation.

The fabrication of layered structures consisting solely of silicon (carbo)nitride was possible on both support types. A continuous crack-free composite layer with a thickness of approximately 30  $\mu\text{m}$  was deposited. Using a masking technique, it was also possible to deposit the selective layer.

### Introduction

Due to their excellent mechanical, thermal and chemical stability, porous non oxide ceramics are interesting materials for use in emerging energy and environmental related fields such as catalysis and separation. Due to the polymeric nature of the precursor, polymer derived ceramics (PDCs) can be prepared using a multitude of processing methods, and thus are flexible in shape. This enables the fabrication of, e.g., ceramic fibers, layered structures, and coatings, which is difficult or even impossible using the powder-based route. There are several ways to influence the porosity of PDCs using for example sacrificial fillers in addition to the porosity evolving during polymer-ceramic-conversion.[1, 2] Layered ceramic structures can be used as asymmetric membranes, which usually consist of a selective layer, responsible for separation, on a macroporous support structure providing mechanical stability. To bridge possible differences in terms of pore size and pore structure as well as varying chemical composition between these two layers, intermediate layers can be used.[3]

The objective of this work was the fabrication of a layered ceramic structure consisting of silicon (carbo)nitride with graded porosity using a dip coating procedure.

### Experimental

**Support structure.** Two types of planar support structures were prepared, serving as substrates for the following layers. Type A supports were prepared using a poly(vinyl)silazane (Durazane 1800, durXtreme GmbH) as polymeric precursor with UHMW-PE spheres as sacrificial filler, yielding amorphous silicon carbonitride.[4] Type B supports were prepared via slip casting and partial sintering of silicon nitride (SN-E10, UBE).

**Intermediate layer.** A combination of the materials of the two support types was used for the intermediate layer. The layer was deposited via dip coating with a slurry containing poly(vinyl)silazane and  $\text{Si}_3\text{N}_4$ -particulates (1:1.4) in toluene. The polymer serves as binder for the particulates, forming a composite layer after pyrolysis. To provide sufficient slurry stability, a silanization treatment of the powder with 3-aminopropyltrimethoxysilane was necessary. By varying the solvent content, a suitable slurry composition was found, yielding continuous crack free intermediate layers, which were investigated using scanning electron microscopy.

**Selective layer.** Dip coating of a poly(vinyl)silazane solution in toluene/n-hexane was used to deposit the selective layer. Preliminary tests were carried out to find the optimum withdrawal speed. By using a masking technique (following the procedure of Hedlund et al. [5]), a selective layer could be deposited. The masking was done using a polystyrene/toluene solution, leading to the use of n-hexane as solvent for the subsequently deposited selective layer. After drying, the pores of intermediate layer and support are filled with solid polystyrene, providing an apparently dense substrate for the deposition of the selective layer. The polystyrene is burnt out during pyrolysis of the poly(vinyl)silazane.

### Results and Discussion

A layered structure with multiscalar porosity was achieved on both of the support types.

The polymer-derived type A supports have a porosity of approximately 42 % with ink bottle-type pores. The slip cast type B supports differ in porosity (~50 %) as well as in pore structure (uniform) when compared to the Type A supports. Fracture surfaces of both support types are shown in

Figure 6. This led to differences in processing of the intermediate layer. A higher solvent concentration of the slurry was necessary on the Type B supports, most likely due to filtration effects. A solvent content of 91 wt% toluene for the slip cast supports and 80 wt% for the PDC supports yielded a continuous and crack-free composite intermediate layer with approximately 30  $\mu\text{m}$  in thickness (Figure 7). After a masking step using polystyrene, deposition of a thin selective layer was achieved on top of the intermediate layer and the porosity of the underlying layers was preserved (Figure 8).

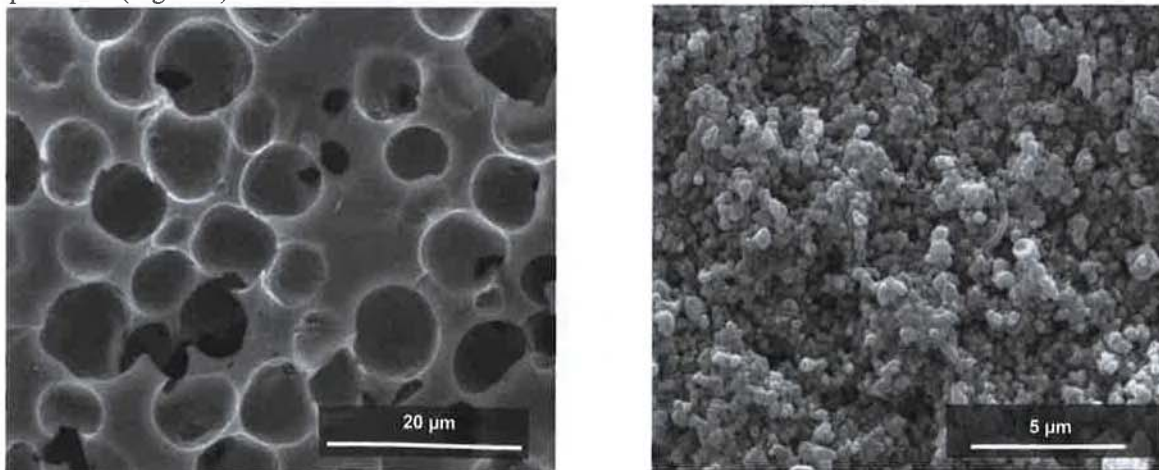
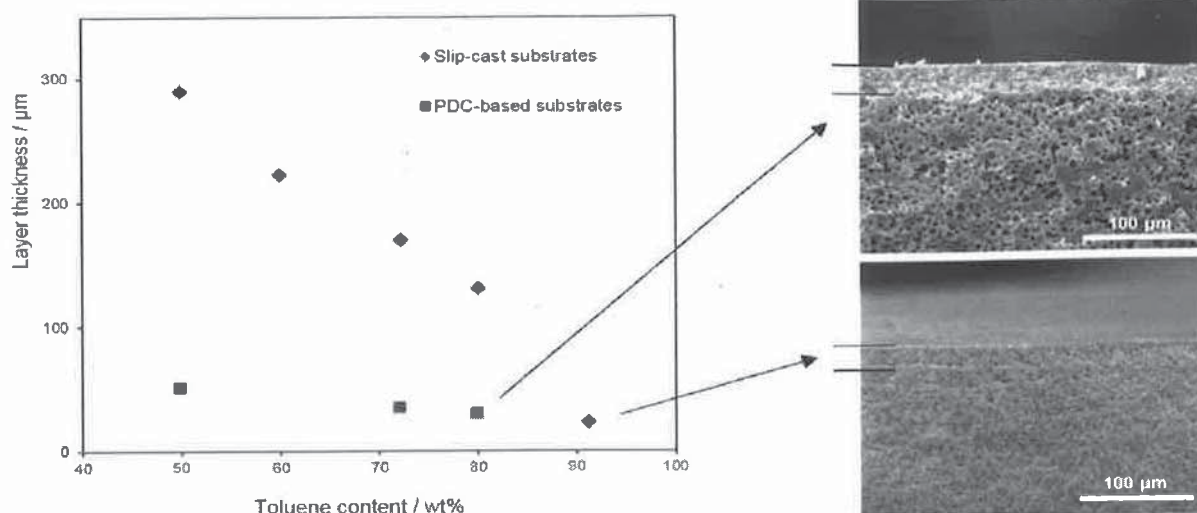
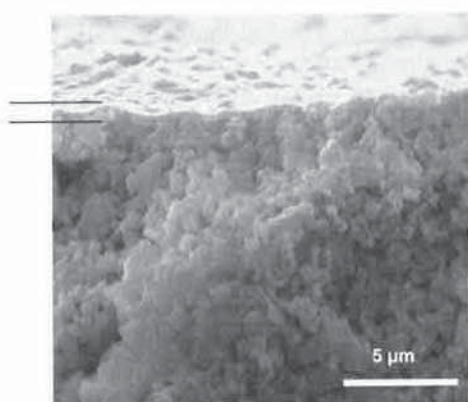


Figure 6: SEM micrographs of fracture surfaces of the PDC supports (left,[6]) and the slip cast supports (right)



**Figure 7: Correlation between solvent concentration and thickness of the intermediate layer (left); SEM micrographs of the intermediate layer on the PDC supports (top) and the slip cast supports (bottom)**



**Figure 8: SEM micrograph of the selective layer on top of the intermediate layer**

### Conclusions

It was shown that it is possible to prepare layered silicon (carbo)nitride structures using a tailored dip coating procedure. A method for the deposition of an intermediate layer as well as a selective layer was developed. Further investigations considering separation characteristics are in preparation.

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# ПРОБЛЕМЫ НЕДРОПОЛЬЗОВАНИЯ

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В сборнике помещены труды молодых исследователей, участников Международного форума-конкурса «Проблемы недропользования» (19-21 апреля 2017 г.). Материалы сборника представляют интерес для широкого круга исследователей, ученых, педагогов, специалистов, руководителей промышленных предприятий и предпринимателей, работающих в области поиска, разведки, добычи и переработки полезных ископаемых.

The Volume contains works of young researchers-participants of International Forum of Young Researchers «Topical Issues of Subsoil Usage», which was held at the St. Petersburg Mining University from the 19<sup>th</sup> to 21<sup>st</sup> April 2017. The Volume can be of great interest for a wide range of researchers, scientists, university lecturers, specialists and managers of industrial enterprises and organisations as well as for businesspeople involved in exploration, prospecting, development and processing of minerals.

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