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Refractory Ceramic Fibres; History and Professional Handling

Heinz Wimmer; DKFG - Deutsche KeramikFaser Gesellschaft e.V.
Philippe Class; ECFIA - European Ceramic Fibre Industry Association

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Introduction

Refractory Ceramic Fibres (RCF) belong to the group of Man-Made Mineral Vitreous Fibres (MMVF) and have been manufactured and used world-wide since 1956 – a period of more than 45 years. Since the Sixties their use in industry has increased as a result of a multitude of positive economic and environmental aspects. This development continues. RCF´s generally consist of aluminium oxide and silicon dioxide fused to make fibres consisting of amorphous ***aluminium silicate***. In some cases this standard chemical composition is supplemented by other oxides, for example zirconia.
The pulverised raw materials are mixed and melted by way of an electric resistance process in a furnace at approximately 2.000 °C [1]. The melt stream coming out of an opening in the furnace bottom is blown or centrifuged to form aluminium silicate fibres. The raw fibres are processed to such products as blankets, boards, shaped parts and textiles in subsequent manufacturing steps.
RCF-products are mainly used for industrial applications, specifically for furnace construction, in a temperature range above 900 °C. These applications improve energy savings of up to 50 % with several additional manufacturing and economical advantages for the user.

Classification and Health Discussion

> ***Was das nit gifft ist?***
> *Alle ding sind gifft und nichts ist ohn gifft.*
> *Allein die dosis macht das ein ding kein gifft ist.*
> *Als ein Exempel:*
> *Ein jetliche speiß*
> *und ein jetlich getranck*
> *so es über sein dosis eingenommen wirdt,*
> *so ist es gifft!*
>
> **Paracelsus**

The discussions about potential health hazards related to man made mineral fibres (MMVF´s), to which RCF´s belong, started in the fifties but only became serious in the early Eighties. Since that time an increasing number of animal experiments and epidemiological tests have been conducted. Up to now no lung disease has occurred in man that can be attributed to RCF´s. This has been confirmed by the results of health studies on workers in the RCF industry . The latest of these were conducted by an renowned institute, the IOM (Institute of Occupational Medicine) [2].

Long term inhalation experiments [3] with rats and hamsters realized at RCC showed that some RCF sample could produce tumours. As a result in 1997 RCF were classified as a carcinogen in category 2 in EU directive 97/69. "*Substances which should be regarded as if they are carcinogenic to humans."*
Today it is known that the results were based on the use of fibre samples which contained many more non-fibrous particles than either the workplace atmospheres or other samples of "man made vitreous fibres" (glass, rock and slag) tested at the same laboratory.

Thus the RCF samples used during these animal experiments were not typical of those in occupational exposures. The combination of fibres and particles overloaded the rat lung's ability to clear particles and this "overload effect" caused chronic inflammation and tumours. This was actually the reason for the increased tumour rate.

During industrial processing of RCF-products there are fibre concentrations of approximately 500,000 F/m^3. This concentration was measured as part of the CARE program thus not only is the exposure to atmospheres qualitatively different from those in the animal experiments, but also containing roughly 300 times lower levels of fibre.
A study of various fibres, at the Fraunhofer Institute in Hanover [Creutzenberg et al 1999] showed that the RCF sample used at RCC caused marked pulmonary inflammation after 3 weeks exposure coupled with all the signs of pulmonary overload.

This study was repeated (Bellmann et al 2001; [4]) with a newly prepared sample of RCF containing only similar levels of particles to those in workplace air samples.
The newly prepared sample had much less impact on the lungs an overload did not occur. This confirmed that the particles in the RCF-sample in the RCC-experiment were essential for the production of overload which in turn could have caused the tumours.

The fibres are not themselves responsible for the formation of tumours and had the samples of RCF tested been prepared by the methods used for the other MMVF samples, it is unlikely that any distinction could be drawn between the different types of MMVF´s: Glass-, Stone- or Refractory Ceramic Fibres.

The conclusion of the Fraunhofer study published in July 2001 is:
The biological activity of RCF, as typically found at work places (not overly contaminated with particles) is similar to that of glass and stone wools. [11]

In October 2001, the International Agency for Research on Cancer (IARC) of the World Health Organisation (WHO) presented a new assessment of MMVF´s.

This new assessment included the latest knowledge of Toxicology [11]. The IARC maintained the classification of RCF in Group 2B "possible carcinogen" as already classified in 1987.

This corresponds to a classification in Category 3 on the European level. A new assessment regarding classification of MMVF and, consequently, RCF in the European Union is scheduled for 2002/2003.

Where are the applications of RCF?

In Europe approximately 50.000 t/a aluminium silicate fibres are manufactured. It represents only 1-2% of the total production of MMVF in Europe (Figure 1). This is, consequently, a very low share.

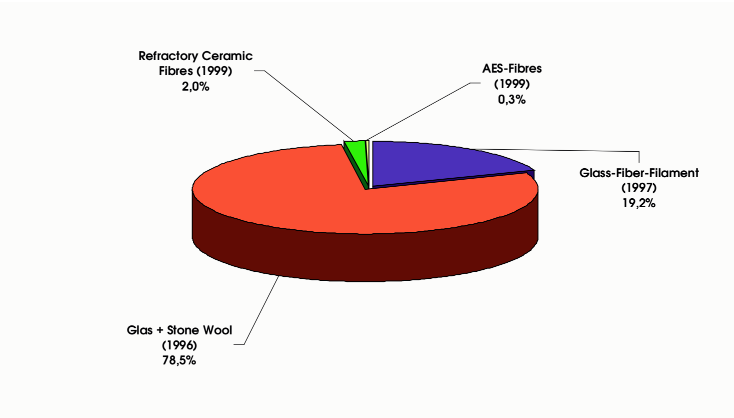

Figure 1: Total production of MMVF in Europe

In contrast to glass and mineral fibres, which are applied in temperature ranges of below 600 °C [5], products out of aluminium silicate fibres are mainly used for industrial applications above 1,000 °C (Figure 2).

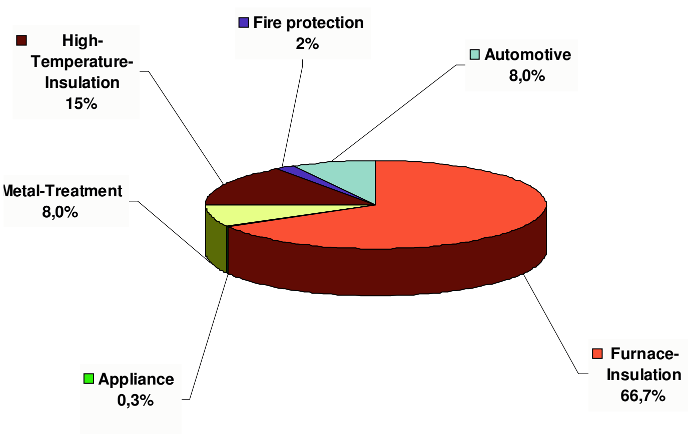

Figure 2: RCF-.Applications

In the steel, non-ferrous metal, automotive, porcelain, chemical and ceramic industries the applications of aluminium silicate fibres in high temperature area up to 1,400 °C have substantial effects on manufacturing processes, productivity and plant flexibility.

This resulted in significantly lower investment costs, reduced consumption of primary energy, operation costs and emissions (i.e. CO_2, etc.) [6].
Due to the primarily industrial applications only a small number of workers are involved in the direct processing of aluminium silicate fibre products.
Generally, trained experts in the refractory and chimney engineering industries work with aluminium silicate fibre products, which are mainly installed as furnace lining.
According to a DKFG estimate approximately 1.500 to 2.000 workers are trained in Germany to work with this product.

<u>Substitute Materials for Aluminium Silicate Fibre Products:</u>

According to legal regulations, classification of a material in category 2 (aluminium silicate fibres are currently in this group) it is required to conduct a substitute search according to § 36 of the dangerous substances regulation (GefStV) [7].
TRGS 619 (Technical Guideline for Hazardous Materials) *“Substitute Materials for Refractory Ceramic Fibres in Furnaces and Refractory Industry“* [5] gives an assistance for the search of substitute materials and legal filing.
Dipl.-Ing. Günter Sonnenschein of the Maschinenbau- u. Metall Berufsgenossenschaft shall give a presentation on this topic at this FF-Colloquium.

Further assistance is provided in VDI-Richtlinie 3469 (Association of German Engineers Guidelines) [1]. Refer to Part 1 in point 2.2. “Substitution“. This document describes rules that should be observed when looking for a substitute for hazardous materials.

<u>Quote:</u>

- *The products´ long term behaviour must be at least equivalent.*
- *Suitability for use of components made of substitution products on existing installations (replacement part service) use.*
- *Availability of sufficient quantities.*
- *Comparable costs.*
- *Substance approval on the basis of product testing-procedures for:*
    - *Safety*
    - *Long term behaviour*
    - *suitability of simulation tests and measures in cases which do not permit such simulations test.*

- *The lower hazard potential of the replacement substance must be sufficiently demonstrated.*
- *Comparable or less severe environmental impact.*
- *Socio-economic aspects.*
- *Recyclability.*

Publications of Dr. Thorsten Bolender [8] and Dr. Gisela Binde [14] clearly illustrate the limited possibilities of substituting aluminium silicate fibres by so-called more biosoluble fibres such as alkaline earth silicate fibres (AES-Fibres).

In summary it can be currently stated that despite intensive research and experiments it was only possible to find a compatible substitute for aluminium silicate fibres in a limited number of applications.
AES-Fibres are mainly used for household appliance industry and fire protection. These are applications where the chemical, thermal and physical conditions are such that AES-Fibres can be used. The application of AES-Fibres is usually not possible in industrial furnace construction.

Below is the summary of a study conducted by the Bundesanstalt für Arbeitsschutz und Arbeitsmedizin (BAuA) [9], which objective was to find substitutes for ceramic fibre products.

<u>Quote:</u>
“As result of the intended objective it can be determined that doing without ceramic fibre products in processes with temperatures above 1,100 °C will cause technical difficulties and limitations. There are, however, application cases where substitution and use of substitute materials is possible because not all of the properties of the ceramic fibres are required. Examples can also be listed that prove that different engineering or design can permit the use of substitute materials for ceramic fibre products. If a substitution of ceramic fibre products is not possible then the design of the products and production must be done in such a way that a release of ceramic fibre dust is prevented to the greatest extent possible. This calls for corresponding occupational safety measures for carcinogenic materials according to the laws governing hazardous materials and TRGS 521 “Fibre dusts” (Technical Guideline for Hazardous Materials).

Consequently, at the moment and based on current judgement there will not be any alternatives in the near future in regard to application of aluminium silicate fibre products in high temperature areas above 1,100 °C. The newly developed AES-Fibres have their limitations for high temperature applications – specifically if in periodic operations. These limitations are related to *chemical and physical resistance* and thus AES-Fibres can only be considered a supplement to the existing aluminium silicate fibre products for few applications. A document referring to the research of a substitute for aluminium silicate fibre can be produced by using the new TRGS 619 [5].

<u>**Professional Handling of Aluminium Silicate Fibres**</u>

Since the 1997 European category 2 classification for *substances and preparations,* such as loose wool made of aluminium silicate fibre and dry cements containing aluminium silicate fibres, must be labelled accordingly. Already, since 1985 DKFG/ECFIA members have voluntarily labelled their products and articles . Even though aluminium silicate fibres *articles* do not need to be labelled, DKFG and ECFIA members continue to voluntarily mark their products with labels and handling advice.

DKFG and ECFIA members inform customers and users since the early Eighties by means of EU Material Safety Data Sheets (MSDS), publications and packaging label, providing information allowing to ensure safe handling of refractory ceramic fibre products.

Since 1996 the Technische Regel für Gefahrstoffe TRGS 521 (Technical Guideline for Hazardous Materials; *"Fibre Dusts"*), which is published by the Ministry of Labour in the official Journal provided by this Ministry, is used as benchmark for safe and professional handling.

The information work of DKFG and ECFIA as well as labelling and handling information were and still are considered as exemplary in industry according to the representative of the Ministry of Labour.

The CARE program [11] is now in its sixth year and proves that, with information on correct handling and with properly installed technical equipment (proper ventilation and filtration systems), it is possible to significantly reduce exposure to fibres.
The limit value of 500.000 F/m³ may be reached in a number of applications. However, during installation and demolition work it is often not possible to remain below this concentration. Consequently, in such cases the required protective measures (protective clothing, breathing mask FFP3) need to be implemented.

Environment:

The unique insulation properties of High Temperature Insulation Wools (HTIW), to which aluminium silicate fibres and alkaline earth silicate fibres belong, enable energy savings up to 50 % at high temperatures in comparison to standard refractories such as bricks and castables.
Considering increased pressure on specific countries, governments and industry to reduce greenhouse gases, the contribution of aluminium silicate fibre products to energy savings is of great importance [6]. Today, reduced energy consumption, related to HTIW-product use, corresponds to a reduction of CO_2-emissions in Europe of more than 10 million t/a with growing trends.

The advantages of aluminium silicate fibre linings for periodic operation of industrial furnaces cannot be stressed enough [13]. These advantages contribute greatly to securing the production location especially of the specific user industries. The expected trade of CO_2-certificates will certainly effect a growing number of applications of aluminium silicate fibre products in the future. Today users already benefit tremendously from achieved reductions.

Summary:

Since the Fifties refractory ceramic fibre products have been manufactured by industry and since the Sixties their use in heat insulation in high temperature applications has increased more and more.

The new technical developments in industrial furnace engineering as well as in energy saving, became possible only with the use of aluminium silicate fibre products. It is no longer possible to do without these products for modern high temperature applications.

In epidemiological studies, which were conducted in 1985 and 1997/98 no ill health effect in man related to exposure to aluminium silicate fibres could be found.

The RCC animal experiments conducted with very high exposure (200.000.000 F/m³) to very fine fibres and particles were used as a basis for European classification.

Later on, studies of the Fraunhofer Institute showed that an “overload effect“ had occured in the RCC-study, and which therefore shouldn´t have been taken into consideration for classification purpose.

IARC considered both studies in their assessment made in 2001 and decided to classify aluminium silicate fibres in Group 2B which is comparable to a classification in category 3 in Europe.
Consequently, the re-classification of aluminium silicate fibres in category 3 should be reconsidered in Europe.

Aluminium silicate fibres are mainly used in industry by approx. 2.000 trained workers. Proactive occupational safety measures in addition to workers´ information and training is a major contribution to lower the potential risk.

Today there is no substitute to aluminium silicate fibre products in high temperature ranges above 1.100 °C [9]. New developed fibres are less biopersistent but have limitations in high temperature applications (above 900 °C) in furnaces operated periodically [8; 12; 14]. These limitations are physical stress and chemical resistance. The AES-Fibres can thus only be used as alternative products to existing aluminium silicate fibres in few cases. Considering all aspects, and in particular economical, environmental and social-economical considerations, one cannot do without aluminium silicate fibre products in a modern plant, if there are heat insulation requirements above 900 °C.

According to statements of Prof. Dr. Ing.Vorath, who conducted the study to find alternatives for aluminium silicate fibres upon the request of the Federal Institute for Occupational Safety and Medicine [9], there will be a growing number of new applications in the future requiring the sole use of aluminium silicate fibre products based on their unique properties.
<u>Quote:</u>
Modern industrial furnace engineering without aluminium silicate fibre products is unthinkable today! [13].
Aluminium silicate fibre products are “High-Tech-Products” which can be applied safely when TRGS 521 and TRGS 619 rules are observed.

The great number of advantages of aluminium silicate fibre products in regards to low energy consumption, investment volume and operational safety will help to secure the production sites of the user industries.

As an example a comparison of different furnace linings in a forging furnace is given below.

Example: Forging Furnace

Gas-Fired: Periodic furnace; 212 m² furnace-lining
Cycles: 48-times/a; 4700 operating hours/a;
Firing temperature: 1300°C

Furnace-Lining		heavy	light	fibre
Specific stored heat	MJ/m²	317,82	330,35	45,33
Operating costs (Energy only)	€/m²/a	414,27	214,22	121,04
Total costs	€/m²/a	502,96	292,52	179,59
Energy-consumption + CO_2-Emission	%	+ 70%	+ 58%	Basis

References:

[1] VDI-Richtlinie 3469, Blatt 1 „Emissionsminderung faserförmiger Stäube“; (October 1998) und Blatt 7 „Keramikfasern“

[2] IOM-Report TM/99/01; Epidemiological Research in the European Ceramic Fibre Industry 1994-1998; Institute of Occupational Medicine (IOM); June 1999

[3] Mast et al; “Studies of the Chronic Toxicity (Inhalation) of four types of Refractory Ceramic Fiber in Male Fischer 344 Rats”; Inhal. Toxicol. 7, 425-467

[4] Bellmann et al, Fraunhofer Institut; Short-term Inhalation study with RCF1a in rats; Hanover July 2001

[5] Technische Regel für Gefahrstoffe; TRGS 619: „Ersatzstoffe für Keramikfasern im Ofen- und Feuerfestbau“; Bundesarbeitsblatt 2002

[6] „High Temperature Insulation Wool Reduces Industries Impact on the Environment“ DKFG; 2002

[7] Gefahrstoffverordnung § 36 Abs. 2 Ermittlungspflicht, (Substitutionsverpflichtung)

[8] Untersuchungen zur Temperaturstabilität von „biolöslichen“ Keramikfasern im Vergleich zu Keramikfasern des Systems Al_2O_3-SiO_2; GASWÄRME International (50) Nr. 9/2001: Fachberichte, Dr. Thorsten Bolender;

[9] „Keramikfaser Ersatzstoffe, Ersatzverfahren, Schutzmaßnahmen.“; Bundesanstalt für Arbeitsschutz und Arbeitsmedizin; GA 52; 1997.

[10] CARE-Program; ECFIA web-site: www.ecfia.org and www.dkfg.de, since 2000

[11] „Exposition gegenüber künstlichen Mineralfasern“; P. Class; R.C. Brown, Gefahrstoffe Reinhaltung der Luft; 2002 Nr. 5 Mai

[12 „Hochtemperaturglasfasern: Ersatz für Keramikfasern?“; Mitgliederzeitschrift der Berufsgenossenschaft Maschinenbau: “Sicher arbeiten!“ 01-2002, Dr. Gisela Binde

[13] Refratory Materials in Ceramic Kiln Construction: Past, Present, and Future CN Refractories Vol. 5-2001; J. Mendheim

[14] Dr. Gisela Binde; Rekristallisierung und Cristobalitbildung in Hochtemperaturglasfasern (AES) nach thermischer Belastung; Gefahrstoffe Reinhaltung der Luft; 62(2002) Nr.6-Juni