Forschungszentrum Karlsruhe
Technik und Umwelt

Wissenschaftliche Berichte
FZKA 5502

Radiation Resistant and Decontaminable Coatings for Shipping, Interim Storage and Repository Storage Casks Containing Radioactive Wastes

S. Kunze, H. Geiser
Institut für Nukleare Entsorgungstechnik

Februar 1995

Forschungszentrum Karlsruhe
Technik und Umwelt
Wissenschaftliche Berichte
FZKA 5502

Radiation Resistant and Decontaminable Coatings for Shipping, Interim Storage and Repository Storage Casks Containing Radioactive Wastes

Siegmar Kunze, Heinz Geiser*
Institut für Nukleare Entsorgungstechnik

Translated by Gertrud Kronimus

*Gesellschaft für Nuklear-Service mbH, Essen

Forschungszentrum Karlsruhe GmbH, Karlsruhe
1995

Forschungszentrum Karlsruhe GmbH
Postfach 3640, 76021 Karlsruhe

ISSN 0947-8620

Radiation Resistant and Decontaminable Coatings for Shipping, Interim Storage and Repository Casks Containing Radioactive Wastes

Abstract

All the Corrobesch-DF-Nuklear coatings - black, yellow, blue, red and white - have been excellently decontaminable without and after radiation exposure with 3 x 10^5 Gy, despite the slightly higher absorbed dose rate applied at KFA Jülich (DIN 55 991 requires $\leq$ 1.0 KGy/h).

After a further increase to 3 x 10^6 Gy in the absorbed dose, with an absorbed dose rate up to 1.0 KGy/h conforming to the standard, the coatings black, yellow, blue were still excellent in their decontamination behavior. After exposure to 10^7 Gy all coatings irradiated at Gammaster in their irradiation room (150 m^3) with permanent air changes and at absorbed dose rates of 0.9 - 1.0 KGy/h have been well decontaminable, and the coatings irradiated at KFA Jülich in the 10 l vessel with discontinuous air changes and variable absorbed dose rate (0.22 - 2.7 KGy/h) have still been fairly well decontaminable only.

To be able to evaluate possible changes occurring upon 10^7 Gy radiation exposure, the test specimens were exposed to the action of chemicals according to DIN 55 991 as well as to decontamination cleansing solutions. Different discolorations, very small reductions in brilliancy, and sometimes minor deteriorations in surface hardness occurred.

Detrimental visible changes, e. g. bubble and crack formation, swelling, detachment from the base, etc., have not been found for any of the coatings. These results for the test specimens irradiated at Gammaster are identical with the results for the test specimens irradiated at KFA Jülich, except minor deviations.

Contrary to expectations, Corrobesch-DF-Nuklear has proved to be a coating material, which, although it consists of organic base material, nevertheless tolerates radiation exposures without visible damage, i. e. conditions under which only electrodeposited nickel coatings have appeared appropriate until now. This means that application of Corrobesch-Nuklear-DF allows the costs of coating of fuel element shipping and storage casks to be reduced.

Strahlenbeständige und dekontaminierbare Beschichtungen für Transport-, Zwischenlager- und Endlagerbehälter radioaktiver Abfälle

Zusammenfassung

Die Corrobesch-DF-Nuklear-Beschichtungen schwarz, gelb, blau, rot und weiß waren alle ohne und nach Strahlenbelastung mit $3 \cdot 10^5$ Gy, trotz etwas höherer Energiedosisleistung in der KFA Jülich (DIN 55 991 fordert $\leqq$ 1,0 KGy/h), sehr gut dekontaminierbar.

Nach weiterer Steigerung der Energiedosis auf $3 \cdot 10^6$ Gy bei normgerechter Energiedosisleistung bis 1,0 KGy/h waren die Beschichtungen schwarz, gelb, blau noch sehr gut. Nach 10^7 Gy waren alle bei Gammaster im Bestrahlungsraum (150 m^3) bei kontinuierlichem Luftdurchsatz und Energiedosisleistung von 0,9 - 1,0 KGy/h bestrahlten Beschichtungen gut und die in der KFA Jülich im 10 l-Behälter bei diskontinuierlichem Luftdurchsatz und schwankender Energiedosisleistung (0,22 - 2,7 KGy/h) bestrahlten Beschichtungen nur noch mäßig dekontaminierbar.

Zur Beurteilung eventueller Veränderungen nach 10^7 Gy Strahlenbelastung wurden die Prüfkörper der Einwirkung von Chemikalien nach DIN 55 991 und Dekontaminationsreinigerlösungen ausgesetzt. Es ergaben sich unterschiedliche Farbänderungen, sehr geringe Glanzverluste und teilweise Minderungen der Oberflächenhärte.

Nachteilige sichtbare Veränderungen, wie Blasen-, Rißbildung, Quellung, Abheben vom Untergrund etc., wurden bei keiner Beschichtung festgestellt. Diese Ergebnisse der bei Gammaster bestrahlten Prüfkörper sind mit den Ergebnissen von in der KFA Jülich bestrahlten Prüfkörpern bis auf ganz geringe Abweichungen identisch.

Wider Erwarten wurde mit Corrobesch-DF-Nuklear ein Beschichtungsmaterial gefunden, welches aus organischem Basismaterial besteht und dennoch Strahlenbelastungen ohne sichtbare Beschädigungen übersteht, für die bisher galvanisch aufgetragene Nickelbeschichtungen geeignet erschienen. Somit kann durch die Verwendung von Corrobesch-Nuklear-DF eine Reduzierung der Kosten für die Beschichtung von Brennelementtransport- und -lagerbehältern erzielt werden.

Contents

1. Introduction

On account of the harmful effects of ionizing radiation, radioactive wastes should be removed from the area of activity of man and from his environment. After conditioning into a solid or solidified product they are enclosed into waste packages [1] and are to be stored in deep geological formations (e. g. salt mines) [2] reserved for this purpose. However, since no repository storage facility for immediate storage had been and is being available in Germany, the waste packages must be kept in above-surface interim stores for some period of time. During that term, the subsequent transport into the repository, and during the operating phase of the repository damage to the waste packages must be sufficiently restricted. Therefore, the standard steel casks, containers, etc. used are provided with long-term resistant paints and coatings, respectively, both inside and on the external side in order to avoid corrosion to develop on the waste packages. The waste packages (repository packages) to be transferred into the repository must be free of corrosion. The external coating of the cask is exposed above all to mechanical loading in the course of shipping, piling up and interim storage of the waste packages. Besides, any damage resulting from chemical interaction with the environment in the store (corrosion), from temperature differences and radiation must be avoided. Obviously, packages undergoing contamination should be well decontaminable too [3, 4]. Besides exhibiting adequate radiation and heat resistance, the inside coating should withstand chemical interactions with the waste forms (cemented wastes, plastic wastes, etc.). The formation of H_2 which is frequently caused by corrosion and the resulting pressure buildup in the package are intolerable. Compliance with the foregoing requirements must be verified before repository packages are stored either in the interim store or in the repository.

Therefore, the coatings used for waste packages must satisfy strict quality criteria. In the following examination of the coating systems priority will be given to these features:

- mechanical stability (cross cutting),
- radiation tolerance,
- chemical resistance to chemicals and decontamination solutions, and
- good decontaminability even after irradiation of the coatings.

The corrosion studies on painted "standard steel casks" during interim and repository storage of low-level wastes [5] demonstrated that in epoxide resin-coated steel casks with undamaged coatings no attack of the base material had taken place in a number of corrosive media. If, however, improper handling of the casks causes penetrating damage of the coating system, corrosion attack and pitting corrosion by underfilm rusting/rust creep must be anticipated. Impact tests with various rock samples used to fill the cavity left between the waste packages and the rock (Konrad Repository Project) have shown that suitable grain sizes of the backfill contribute to minimizing damage to tar-epoxide-polyurethane coated waste packages [6].

The corrosion studies with Corrobesch-DF-Nuklear coated metal casks will not be reported here because this has been a proven coating for a long time in shipbuilding and has exhibited good corrosion behavior in sea water. This is confirmed by corrosion tests made on these coatings [7].

In the present studies the radiation resistance and decontaminability of this corrosion resistant coating material will be discussed.

The reasons underlying these studies are

(1) the increasing activity inventory of the presently conditioned waste packages due to storage costs calculated on the basis of volumes;

(2) the potential use of possibly less costly inner coatings substituting the expensive metal inner coatings presently applied in fuel element shipping casks, and

(3) the use of novel radiation resistant material in nuclear engineering buildings exposed to high doses.

2. Studies

2.1 Specimens

50 mm x 50 mm x 3 mm steel sheets were used as specimen carriers.
The coating material consists of the basic component A (tar-epoxide-polyurethane and inert additives as well as pigments) and the component B (cycloaliphatic amine). Corrobesch-DF-Nuklear is a duroplastic two-composite coat-

ing material with average Poisson number which is tight to water vapor diffusion and free of solvents.

The solvent-free product was applied with a two-composite airless spraying system with heater (temperature ~ 70 °C). An approx. 1000 µm coating was applied on both sides of the steel sheets. The specimens were cured at ambient temperature.

2.2 Irradiation

After four weeks of curing at ambient temperature (DIN 50 014) the coatings were exposed to ionizing radiation. The test was made in accordance with DIN 53 781 (presently being revised) up to an absorbed dose of 10 MGy (1 x 10^9 rad) and gamma irradiation in air. Two different irradiation sources were used for irradiation.

The irradiation with Co-60 radiation sources was carried out at Gammaster München in rooms (about 150 m^3 volume) with permanent changes of air (about 10,000 m^3/h). The distance between the Co-60 radiation source and the specimen plates was chosen such that the absorbed dose rate was 0.9 - 1.0 KGy/h. The ozone content in the air was monitored; it attained approx. 0.5 ppm (Table 2).

Irradiation in a mixed gamma field was performed at KFA Jülich in an open vessel within the basin (irradiation basin) in air atmosphere. The fuel elements arranged in the MTR annular gap emit radiation having the same spectrum as a complete fission product mixture. During irradiation of the specimens the air in the irradiation vessel was changed four times a day. Every time the 10 l irradiation vessel was flushed with 100 l air. The air supply tube extended to 1 cm above the bottom of the irradiation vessel. The absorbed dose rate was 0.22 to 2.7 KGy/h. Consequently, it partly exceeded the maximum absorbed dose rate of 1 KGy/h recommended for nuclear facilities.

2.3 Contamination and Decontamination of the Specimens

The tests were made in conformity with DIN 25 415, Part 1, whose contents are identical with ISO 8690. The irradiated and the non-irradiated test specimens were contaminated with the radionuclides Cs-137 and Co-60, which had been applied in separate solutions.

The decontaminant used in the tests was deionized water at a temperature of (23 ± 2) °C and a maximum conductivity of 3 µS/cm. Deviating from DIN, only two to three test specimens were exposed to each radionuclide instead of five.

3. Results

3.1 Visible Changes in the Coatings

A visual evaluation was made by comparison of the non-irradiated with the irradiated test specimens.

The system applied to evaluate the irradiated test specimens was the relative grading scale according to DIN 53 230.

Reference Number	Explanation
0	no change
1	minimal changes
2	little changes
3	moderate changes
4	strong changes
5	very strong changes

Radiation exposure of the test specimens to 10^7 Gy results in

- discolorations of different intensities
  (most intensive for white coating, reference number 4,
  least intensive for black coating, reference number 1), and
- very slight reduction in brilliancy (reference numbers 0 - 1).

Other changes such as bubble and crack formation, swelling, chalking, etc. have not been observed. The results obtained for the test specimens irradiated at Gammaster München, are identical with those obtained at KFA Jülich.

The hardness of coating slightly decreases with increasing absorbed dose. As the test specimens had not been available immediately after irradiation, no evaluation is being made here.

3.2 Resistance to the Action of Chemicals and Decontamination Solutions

To be able to evaluate possible changes upon the action of chemicals and decontamination solutions on irradiated Corrobesch coatings the test liquids ethanol, 20% phosphoric acid and caustic soda solution, the material testing mixture A 20/NP II and, in addition, two decontamination cleansers frequently used in practice, all of them listed in DIN 55 991, Part 1 (Requirements on Coatings for Application in Nuclear Facilities) were applied according to DIN 53 168, Section 7.2, to test specimens irradiated at different absorbed dose rates. The changes of the coating surfaces were evaluated after 5 minutes and after 24 hours of action.

The results are compiled in Table 2. They make evident that

- after 5 min. of action non-exposed surfaces as well as those irradiated with radiation doses up to 10^7 Gy exhibit but negligible changes upon the action of the solutions above (color and hardness, reference numbers 0 - 1), independent of the pigment used;
- after 24 h of action all surfaces exhibit minor changes upon the action of the material testing mixture A20/NP II and of the two water-diluted decontamination cleansing solutions (color and hardness, reference numbers 0 - 1);
- after 24 h of action of ethanol, phosphoric acid and caustic soda solution the discoloration increases with growing radiation exposure of the surface, and the hardness of the coating decreases temporarily (the white coating yielded the poorest values, reference numbers up to 4).

Other changes, e. g. bubbles, cracks, swelling, etc. due to the action of the solutions above have not been observed on any of the specimens irradiated up to 10^7 Gy. Also in this case, the results obtained for the specimens irradiated at Gammaster München are identical, except for minor deviations, with those obtained for the specimens irradiated at KFA Jülich.

3.3 Results of Decontamination

The results of decontamination of Corrobesch-DF-Nuklear coatings with five different pigments without and after irradiation up to absorbed doses of 10^7 Gy, performed at Gammaster at constant absorbed dose rate (0.9 - 1.0 KGy/h), have been compiled in Fig. 1 and those obtained at KFA Jülich at variable absorbed dose rates (0.22 - 2.7 KGy/h) have been compiled in Fig. 2.

All test specimens - black, yellow, blue, red, white - are very well decontaminable before they are irradiated.

Irradiation with 3 x 10^5 Gy: All test specimens irradiated at Gammaster and KFA Jülich are very well decontaminable. Consequently, they satisfy the requirements made on coatings for use in nuclear facilities (DIN 55991).

Irradiation with 1.7 x 10^6 Gy: The test specimens (black, yellow, blue) are very well and the test specimens (red and white), all irradiated at Gammaster, are well decontaminable. All specimens irradiated at KFA Jülich are well decontaminable.

Irradiation with 3 x 10^6 Gy and 6.8 x 10^6 Gy: For these decontamination tests only test specimens were available which had been irradiated at Gammaster. Despite higher Co/Cs residual pulse rates, the evaluation of the test specimens irradiated with 3 x 10^6 Gy yields the same result as that for specimens irradiated with 1.7 x 10^6. All coatings irradiated with 6.8 x 10^6 Gy are also well decontaminable.

Irradiation with 10^7 Gy: All test specimens irradiated at Gammaster are well, all specimens irradiated at KFA Jülich are fairly well decontaminable. Surprisingly, all Cs values are always higher than the Co values irradiated with that and higher absorbed doses.

The longer the test specimens had been irradiated prior to decontamination, the higher were the Co/Cs residual pulse rates which means that the decontaminability decreased from excellent to fair in some cases. The Co/Cs residual pulse rates which, for the absorbed dose of 1.7 x 10^6 Gy and above, have always been higher for the coatings irradiated at KFA Jülich than for the coatings irradiated at Gammaster are probably attributable to the very small irradiation vessels, with only discontinuous air changes, used at KFA Jülich and maybe also to the absorbed dose rates attaining values up to 2.7 KGy/h. (Table 1).

4. References

[1] P. Brennecke, E. Warnecke
Anforderungen an endzulagernde radioaktive Abfälle,
Bundesamt für Strahlenschutz ET-3/90, Salzgitter (April 1990).

[2] A.G. Herrmann, B. Knipping
Stoffbestand von Salzstöcken und Langzeitsicherheit für Endlager radioaktiver Abfälle,
Physikalisch-Technische Bundesanstalt Braunschweig,
SE 1/89.

[3] S. Kunze, G. Lösch, F. Österreich, H. Schlautek
Dekontaminierbarkeit von Beschichtungen für ISO-Container,
Atom + Strom 31 (1985), Vol. 6, p. 168.

[4] S. Kunze, H.-R. Schmidt
Verhalten von dekontaminierbaren Beschichtungen vor und nach Belastung mit ionisierender Strahlung,
Atom + Strom 34 (1988), Vol. 4/5, p. 114.

[5] W. Hauser, B. Fiehn
Korrosionsverhalten lackbeschichteter Normalstahlbehälter bei der Zwischen- und Endlagerung,
Bericht KfK 4300 (June 1988).

[6] H.-P. Berg, P. Brennecke, V. Friehmelt
Beschädigung von Oberflächenbeschichtungen bei Aufprall von Gestein
Farbe + Lacke, 96 (1990), Vol. 4, p. 261.

[7] U. Krawietz
Zwischenbericht über Prüfungen an Corrobesch-DF,
Bundesanstalt für Materialprüfung, Berlin, (September 1983).

Table 1: Irradiation of Corrobesch-Nuklear-DF Coatings

	Gammaster München In Room Irradiation	KFA Jülich In Vessel Irradiation
Radiation source	Co-60	spent fuel elements from MTR annular gap; approx. 50% burnup; irradiated in cooling pond
Mean absorbed energy [MeV]	1.17 / 1.33	approx. 0.7
Homogeneity of the radiation field [%]	± 10	± 10
Mean absorbed dose rate [KGy/h]	0.9 to 1 *)	0.22 to 2.7 *)
Absorbed dose [up to MGy]	10	10
Measurement of absorbed dose	red-acrylic und alanine	glass dosemeter, range 1 to 10^6 Gy
Irradiation room (or vessel) [liter]	150.000	10
Test specimen	50 mm x 50 mm x 3 mm	50 mm x 50 mm x 3 mm
Ambient athmosphere	air, relative humidity 30 to 70%	air, relative humidity 50 to 70%
Ozone content during irradiation	~ 0.5 ppm	not measured
Pressure built up in the vessel due to radiochemical reactions	--	not observed open
Temperature of the specimens during irradiation [°C]	15 to 25	28 to 32
Air changes during irradiation	permanent	4 times a day, 10 times the contents of the irradiation vessel per air change

*) in this special case

Table 2: Resistance to Chemicals of Corrobesch-Nuklear DF Coatings according to DIN 53 168 (shading: black, blue, red, yellow, white)

Test Liquid / Tested after	After Irradiation with							
	non-irradiated		3×10^5 Gy		1.7×10^6 Gy		1×10^7 Gy	
	5 min	24 h	5 min	24 h	5 min	24 h	5 min	24 h
Ethanol, 95 vol.%								
color	0	1	1	1-2	1	2-3	1	3-4
hardness	0	0	1	1	1	1-2	1	2-3
bubbles, cracks, swelling, etc.	0	0	0	0	0	0	0	0
H_3PO_4, 20% + wetting agent								
color	0-1	0-1	0-1	0-1	0-1	1-2	1	2-4
hardness	0	0	0	0	0	0	0	1-3
bubbles, cracks, swelling, etc.	0	0	0	0	0	0	0	0
NaOH, 20% + wetting agent								
color	0	1-2	0	2-4	0	2-4	0-1	3-4
hardness	0	0	0	0	0	1-2	0-1	2-4
bubbles, cracks, swelling, etc.	0	0	0	0	0	0	0	0
Material testing mixture A20/NPII								
color	0	0	0	0	0	0	0	0-1
hardness	0	0-1	0	0-1	0	0-1	0	0-1
bubbles, cracks, swelling, etc.	0	0	0	0	0	0	0	0
Papan Dekopan 85, 10%								
color	0	0	0	0-1	0	0-1	0	0-1
hardness	0	0	0	0	0	0	0	0-1
bubbles, cracks, swelling, etc.	0	0	0	0	0	0	0	0
Senzacon-sour, 10%								
color	0	0	0	0-1	0	0-1	0	0-1
hardness	0	0	0	0	0	0	0	0-1
bubbles, cracks, swelling, etc.	0	0	0	0	0	0	0	0

Fig.1: Results of decontamination according to DIN 25415, Part 1 / ISO 8690 obtained prior to and after irradiation of Nuklear-DF coatings of different color shadings

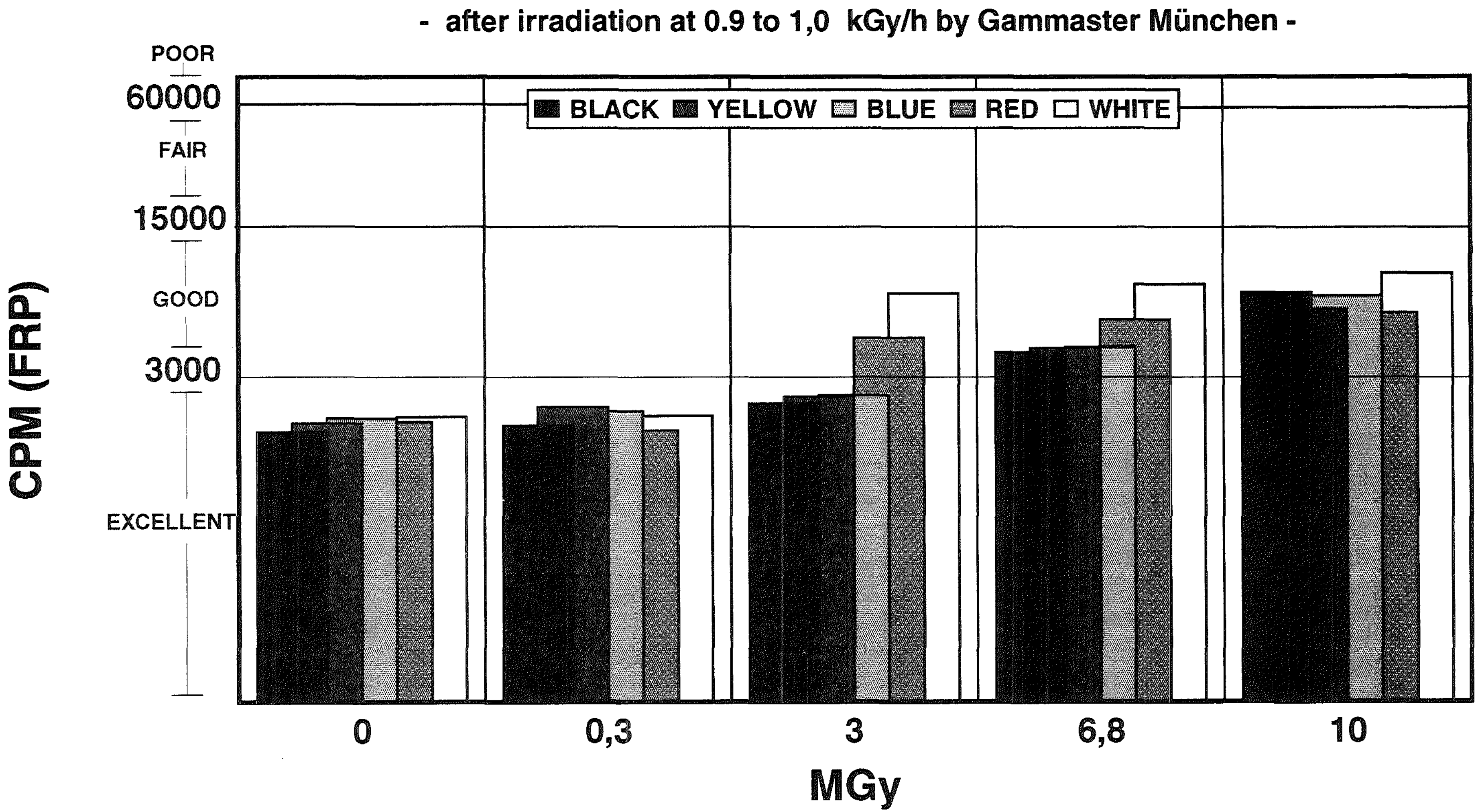

Fig.2: Results of decontamination according to DIN 25415, Part 1 / ISO 8690 obtained prior to and after irradiation of Nuklear-DF coatings of different color shadings