EUROPEAN COMMISSION

Community Research

SEVENTH FRAMEWORK PROGRAMME

CARBOWASTE

Treatment and Disposal of Irradiated Graphite and Other Carbonaceous Waste

Grant Agreement Number: FP7-211333

Technical Report T-2.5.4

Literature compilation on FZJ separation methods

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Date of issue of this report : 26/01/2010

Start date of project : **01/04/2008** Duration : **48 Months**

Project co-funded by the European Commission under the Seventh Framework Programme (2007 to 2011) of the European Atomic Energy Community (EURATOM) for nuclear research and training activities		
Dissemination Level		
PU	Public	
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CARBOWASTE		
Work package: 2 **Task: :** 2.5	**CARBOWASTE document no:** CARBOWASTE-1001-T-2.5.4	**Document type:** T = Technical Report
Issued by: Forschungszentrum Juelich, DE **Internal no.:** CW1001-WP2-T-2-5-4-a		**Document status:** Draft

Document title

Homogeneous Oxidation of Graphitic HTR Fuel Element Matrices

Executive summary

Two high-temperature gas-cooled graphite-moderated reactors, the 15 MWe AVR (experimental nuclear reactor) and the 300 MWe THTR-300 (thorium high-temperature reactor), were operated in Germany. During their operational time about 1 million spent fuel pebbles, each containing some ten thousands of coated particles, were produced [1]. In these reactors, the coated particles with ceramic oxide $(Th,U)O_2$ and UO_2 or carbide $(Th,U)C_2$ kernels were used as the basic fuel-containing units [2]. A closed fuel cycle was originally foreseen also for HTR. Thus, reprocessing of this type of fuel had to be developed, too.

In the former HTR spent fuel reprocessing plant (JUPITER) project, different methods were evaluated to extract the kernels from the coatings. These processes are shortly illustrated.

In the recent RAPHAEL project, the leaching of diverse fuel kernels was investigated. Thus, some few kernels had to be separated from the coatings.

For this purpose, a milling machine was used for cracking the coatings. The fuel kernels were separated from the broken coating by swivelling in water due to the levitation behaviour of the kernels. The remaining pyrocarbon buffer material was removed by an ultrasonic treatment. Approximately 60% of the fuel kernels could by isolated by this procedure without producing broken kernels. The kernels were characterised by optical and electronic microscopy and x-ray diffraction [7].

A comparison of the different segregation methods and a literature compilation are presented, at the end of the report.

Revisions

Rev.	Date	Short description	Author	Internal Review	Task Leader	WP Leader
00	dd/mm/yyyy	Issue	Name, Organisation	Name, Organisation *Signature*	Name, Organisation *Signature*	Name, Organisation *Signature*
01	28/08/2009	First issue	von Lensa FZJ			
02		2nd Issue	von Lensa FZJ			

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1 The JUPITER Project

1.1 Process Description

The Juelich Pilot plant for Thorium Element Reprocessing (JUPITER) was developed in the 1970th with a planned start of operation in 1985. It was a pilot scale demonstration of process and equipment for recovery of decontaminated uranium and thorium from spent high temperature gas-cooled reactor fuel. The capacity was in the range of 2 kg (Th, U) O_2/d. T

Spherical fuel elements of the 15 MWe experimental power station AVR (Arbeitsgemeinschaft Versuchsreaktor GmbH) with a Burnup < 10% fima and a cooling time > 150 d. The removal of the graphite moderator and the pyrocarbon fuel coatings was done by burning with oxygen in case of BISO fuel. For TRISO particles additional separation techniques were discussed because the SiC layer would withstand the burning process.

The spent fuel was converted to a nitrate solution by reaction with F-catalyzed nitric acid. The recovery and decontamination of uranium and thorium was done by liquid/liquid extraction with TBP/n-Dodecan. The final products were uranium and thorium nitrate solutions.

The processing (see Fig. 1) starts with reduction of the spherical fuel elements in a hammer mill to fragments of a size suitable for fluidized-bed burning. The crushed material is fed into a fluidized-bed burner and burnt with oxygen at 800°C-850°C. Fines that escape from the burner are recycled and the off-gas passed through packed-bed adsorbers to remove radioactive contaminants.

The remaining spent fuel, which is in the form of oxides, is dissolved in Thorex-reagent (13 M HNO_3, 0.01 M Al $(NO_3)_3$, 0.05 M HF). The dissolver product, a high molarity nitric acid solution with a thorium concentration of about 1 mol/l, is first passed through filters for clarification and then transferred to the feed adjustment system, where acid stripping is applied to produce a solution corresponding to solvent extraction conditions. Separation of uranium and thorium from each other as well as from the fission products is achieved by tri-n-butyl-phosphate (TBP) extraction. The solvent extraction system of JUPITER was very flexible and permitted testing of various processes like the Acid Thorex process with 30 Vol% TBP/n-dodecane, Interim processes with 5 Vol% TP/n-dodecan and combinations of both.

Besides the main processing steps, auxiliary unit operations were performed, like

- product handling
- solvent regeneration
- nitric acid recycling, and
- clean-up of the dissolver, evaporator and vessel off-gas.

The JUPITER plant was nearly completed before decisions were taken to change from High-Enriched Uranium and Thorium to Low-Enriched Uranium fuel cycles due to Proliferation Issues. However, the Head-end was tested with non-irradiated fuel. Therefore, the JUPITER plant provides a profound technology basis for closing the HTR fuel cycle, even for thorium-based fuel.

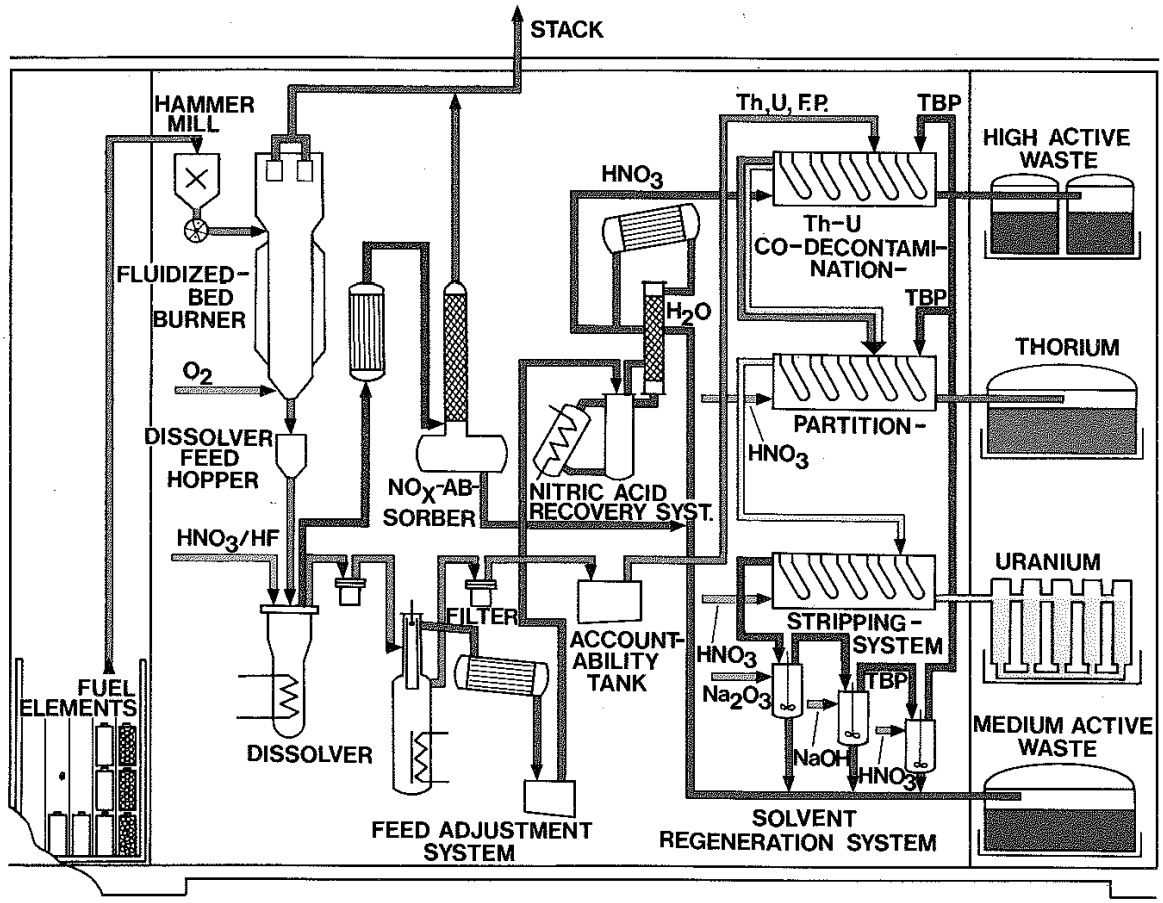

Figure 1: Process Scheme of the JUPITER Plant

1.2 Kernel Extraction from TRISO Fuel

Different processes were investigated to segregate the fuel kernels from the TRISO coatings

- Jet stream method
- Diamond Disk Mill
- Particle Jet Mill
- Double-Roll-Crusher

The principles of these processes are shortly described here and will later be explained in more detail.

In the *jet stream method*, compressed air is injected from the side into a fluidized bed consisting of spent coated particles (CP). The particles are accelerated by the horizontal high-speed jet (Düsenluft) and impinge against a plate on the other side. The SiC layer rupture by this mechanical impact and release the fuel kernel.

In the *diamond disk mill*, the particles are pressed into the mill gap by a butterfly screw. Due to the high tension, the SiC layers will break.

The function of the *particle jet mill* is similar to the jet stream method. However the particles are already accelerated within the injection tube.

In the *double-roll-crusher*, the particles are transported between the two counterrotating rollers. In the mill gap of a defined distance, the particles are crushed and loose their coating layers.

1.2.1 Jet stream method

Beginning of the 1970th, this process (jet grinder) was developed in the US as a new process for separation of the SiC layers of TRISO CP [3]. The function is explained in Fig. 2.

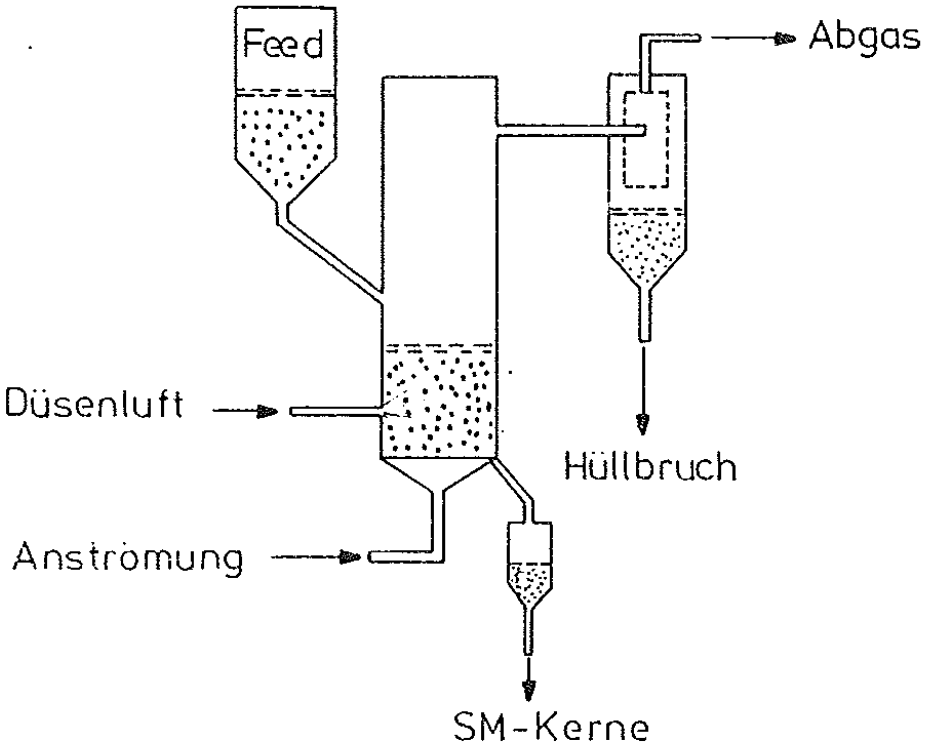

Figure 2: Principle of the Jet Stream Method [4]

The fluidized-bed is sustained by oxidizing gas (Anstroemung). The jet (Duesenluft) reaches nearly sound velocity. Thus the CP are accelerated to high speed and break when impinging the steel plate on the other side of the fluidized-bed.

The particle break rate is dependent on the

- Cross-section of the jet
- The pressure of the jet stream
- The distance to the impact plate.

The benefits of this method as compared to the roll crushers are:

- The whole layers are removed from the kernels
- The fragments of the layers are relatively large
- The maintenance efforts are rather low.

In Germany, this principle was tested in the Forschungszentrum Juelich (former KFA) with a fluidized-bed diameter of 20 mm and 300 mm height. The fluidized bed container was made of glass and the impact plate (Prallplatte) made of steel (see Fig. 3)

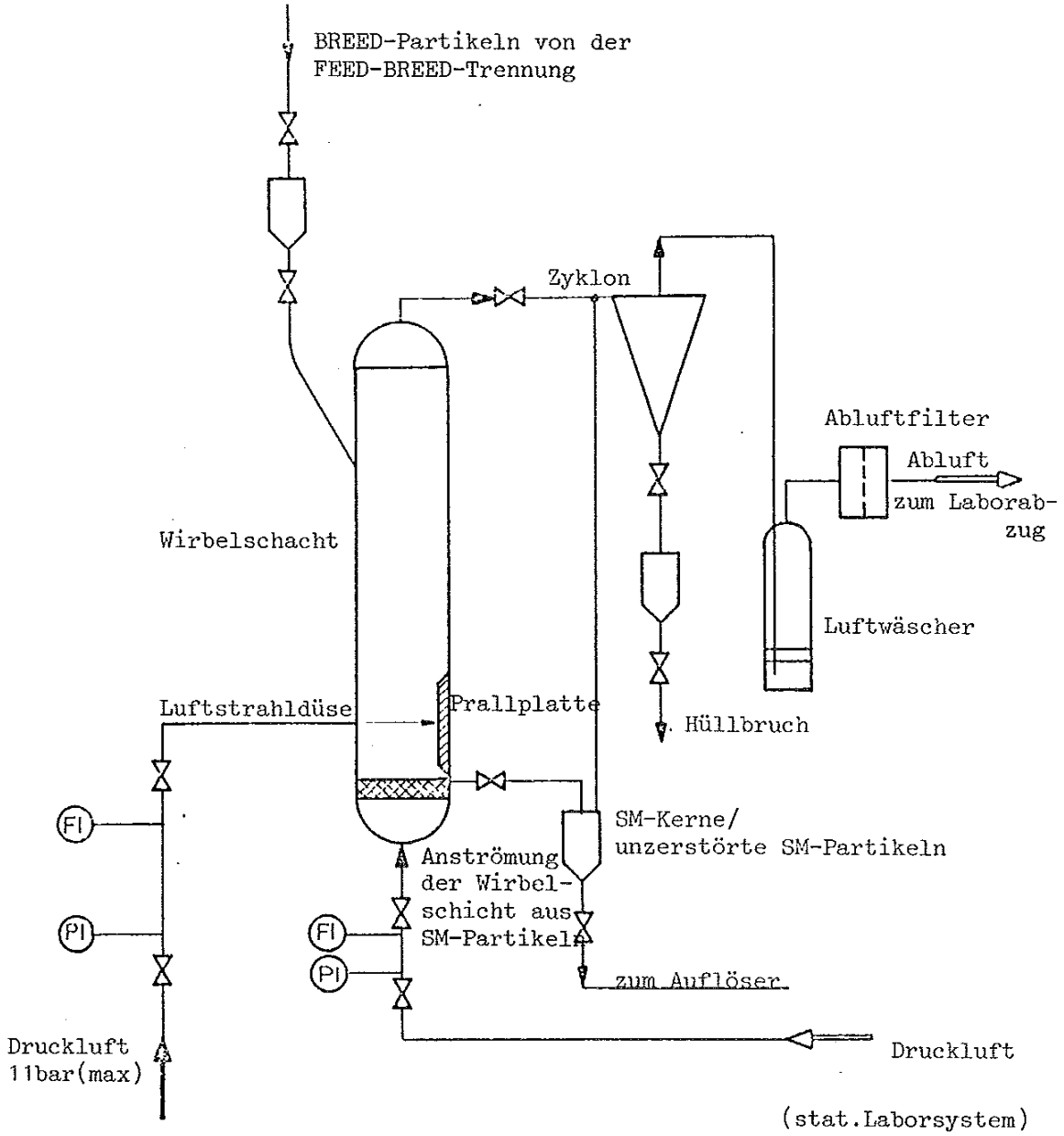

Figure 3: Test facility for the jet stream mill at KFA

The jet stream reached about 300 m/s. The weight of the PyC-SiC layers is lower than the weight of the heavy metal kernels. Thus, the layers can be removed on top of the facility by a cyclone separator and the kernels can be collected from the bottom of the fluidized-bed.

Most tests were made with un-irradiated ThO_2-TRISO particles. 90% of CP were broken after 15 minutes. Another increase by 6% was reached when prolonging the test period to 30 minutes. Good results were achieved by a cross section of the jet of 1mm. UC_2 TRISO CP showed less efficiency probably due to the lower specific weight of the UC_2 CPs.

The dust fraction was in the range of 1% and the heavy metal fraction in the broken layers was between 0,37% and 1,5% depending on the CP origin.

1.2.2 Diamond Disk Mill

Test with a diamond disk mill were also undertaken at KFA [4]. The facility is illustrated in Fig. 4.

The diamond disk mill consists of one rotating disk and one stationary diamond disk. The butterfly screw is turning together with the rotating disk. This arrangement transports the CP into the adjustable mill gap.

The break fraction and the size distribution of the milled CP is only dependent on the size of the mill gap as the turning speed is kept constant.

In all tests, 20 g of CP were inserted.

The dust generation is relatively low (<1,5%) and the size of the dust particle was in the range below 40 micro meter.

The optimum mill gap for ThO_2-TRISO CP with a diameter of 0,8 mm was between 0,55 mm and 0,6 mm.

The optimum mill gap for UC_2 TRISO CP with a diameter of 0,5 mm was between 0,3 mm and 0,4 mm.

Smaller mill gaps increase the fraction rate of the layers to 100% but also augment the fracture rate for the kernels.

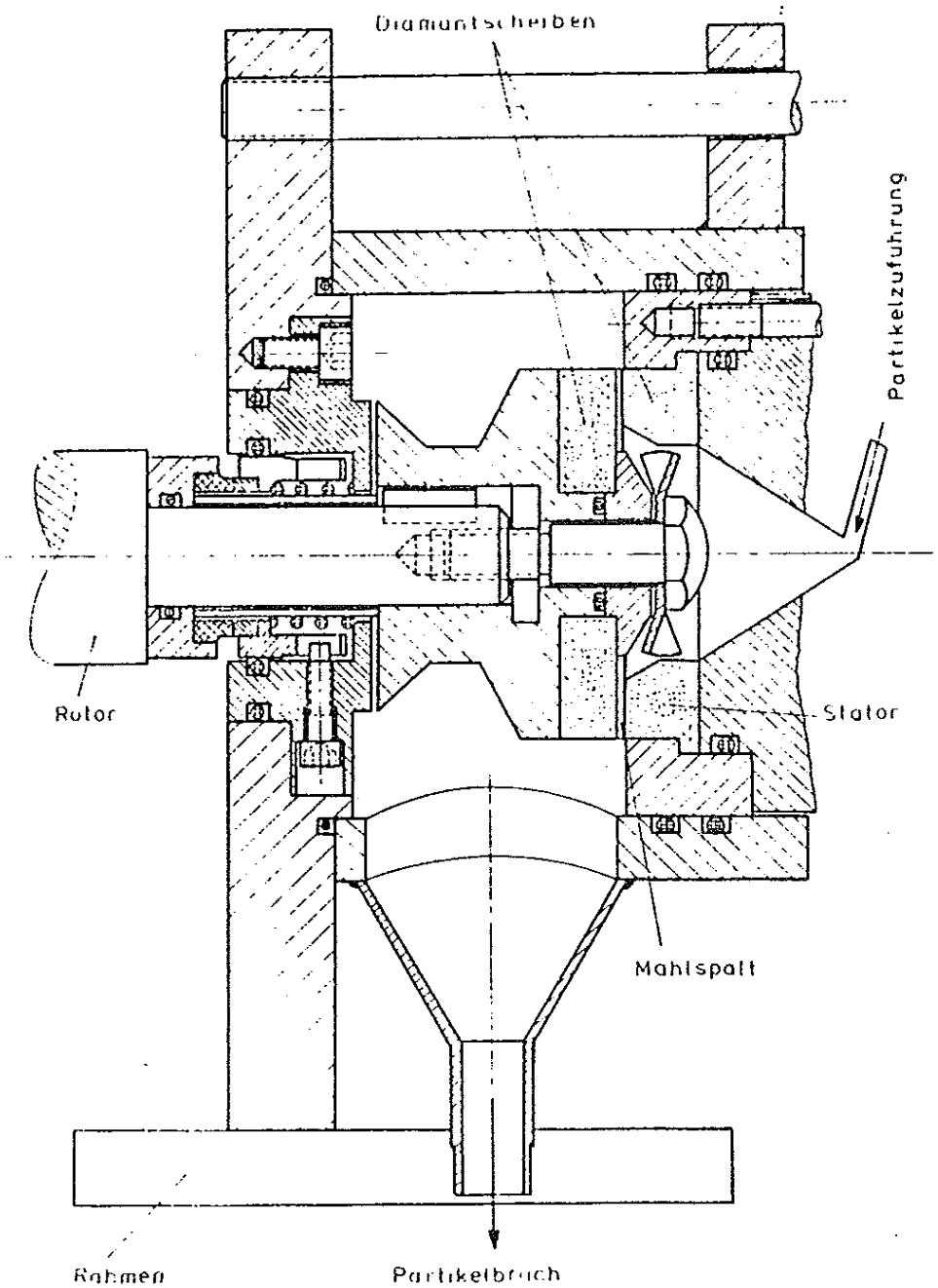

Figure 4: Diamond Disk Mill tested at Forschungszentrum Juelich

1.2.3 Particle Jet Mill

Tests with a particle jet mill were also conducted at the Forschungszentrum Juelich and are described in [4]. The facility is illustrated in Fig. 5.

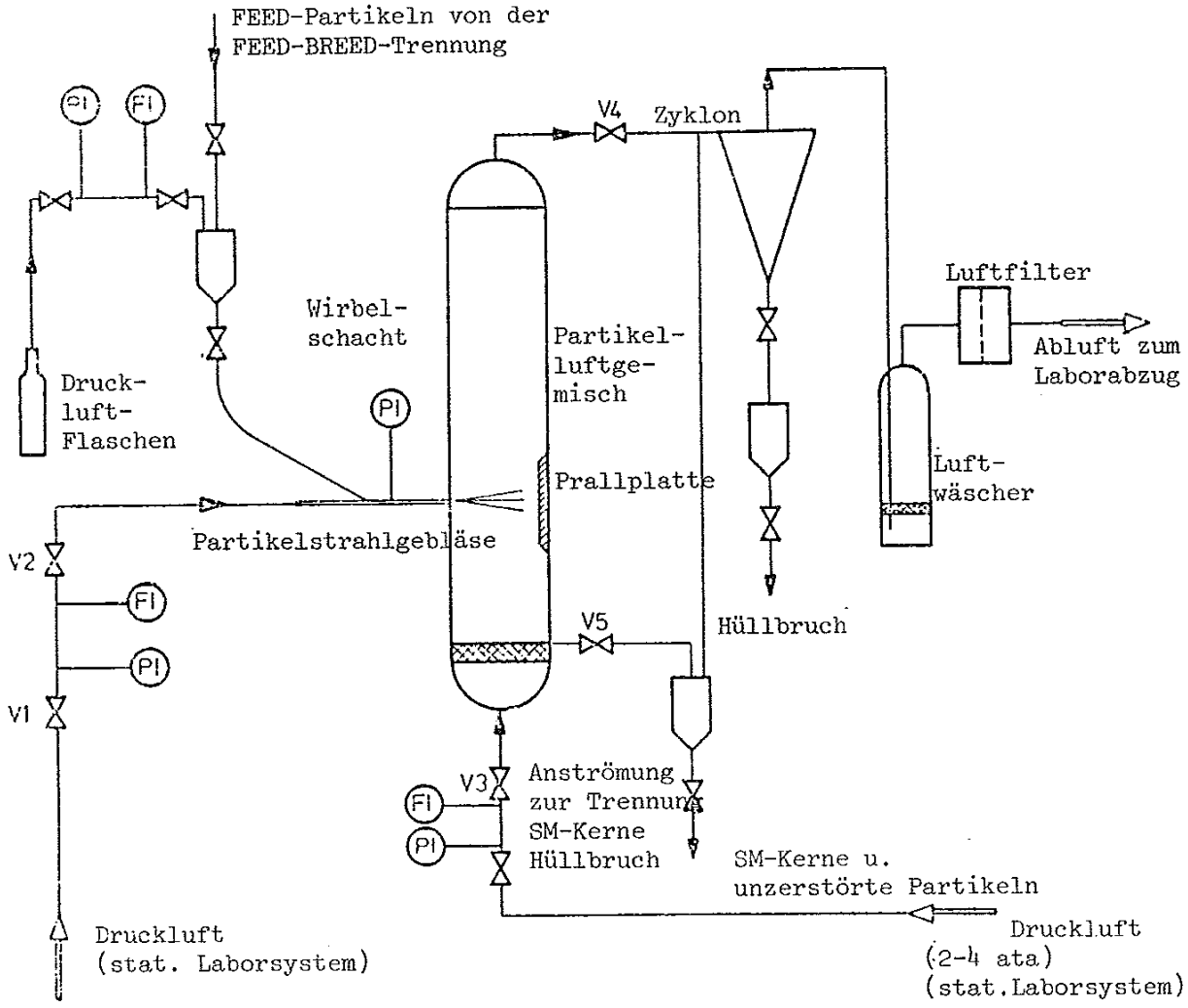

Figure 5: Particle Jet Mill tested at Forschungszentrum Juelich

The facility is similar to the jet stream mill except that the particles are already injected (PI) and accelerated in the jet stream (Partikelstrahlgeblaese). The CP reach high velocities and impinge on the impact plate (Prallplatte). This destroys the coating, which is then carried over into the cyclone separator. The mainly undestructed kernels are accumulating at the bottom of the facility.

Tests were made with ThO_2-TRISO CP and UC_2 TRISO CP.

The results show

- a dependency of the fracture rate on
  - Length of the acceleration distance
  - The pressure of the jet stream
  - The way of injection of the CP.
- Injection of CP by gravity was better than injection by pressure.
- 20 g of CP were milled in 30 seconds.
- Dust fraction was very low (0,2 %)
- Dust size is between 0 -40 micro meter
- The surfaces of the kernels are nearly intact.

1.2.4 Double-Roll-Crusher

The tests of the double-roll crusher was conducted in the US [5, 6]. The facility consists of two 2,5 cm long parallel rolls with an outer diameter of 7,5 cm. The mill gap is 0,43 mm. To reduce generation of fine dust the minimum mill gap should not be smaller than 0,3 mm.

With a mill gap of 0,43 mm about 75% of the kernels of TRISO breed CP (550 -870 micro meter) remain intact.

The throughput of the device is 10 kg of CP per hour.

Another double-roll-crusher as described in [5] had rolls of 10 cm length and 10 cm diameter (see figure 6).

The CP are fed from the feed bunker from above by gravity to the double-roll-crusher and pass the mill gap. The product is then put to the feed bunker of the oven to burn the residua of PyC.

The test were done with

- FSV-Breed CP
- FSV-Feed CP
- LHTGR-Feed CP

	FSV-Breed	FSV-Feed	LHTGR-Feed
Turning speed (UPM)	36-40	43	36
Throughput (kg/h)	50, 101, 148	80	55
Milling gap (micrometer)	480	280	495
Fracture rate (weight %)	> 99%	~97%	>99%

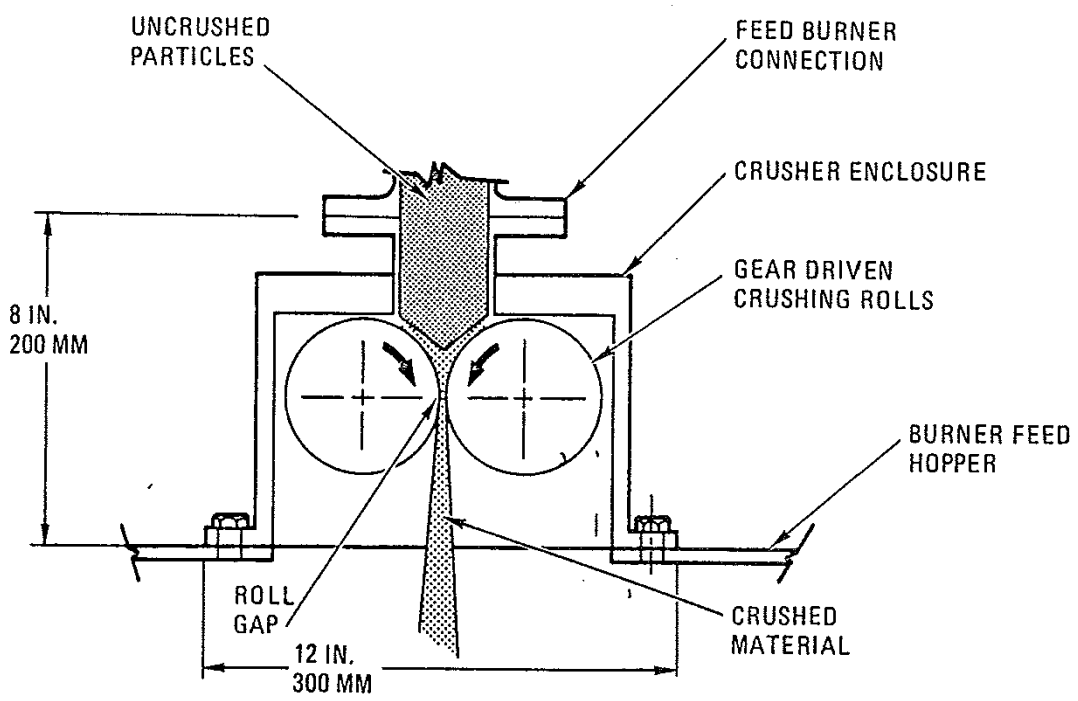

Figure 6: Double-Roll-Crusher [5]

2 Retsch Mill Kernel Extraction from UC_2 TRISO Fuel

2.1 Sample Material

For the recent work within the RAPHAEL project, coated particles from HOBEG were used as source for UC_2 fuel kernels. The container with the coated particles was labelled “UC2 uf15”. The other UC_2-based coated particles could not be used, because the kernels were broken during the isolation procedure.

The coated particles are spherical particles with a diameter of approximately 0.8 mm. For an investigation of their inner structure, the particles were fixed in epoxy resin and thereafter grinded and polished. Photographs of the coated particles sections are presented in Figure 7.

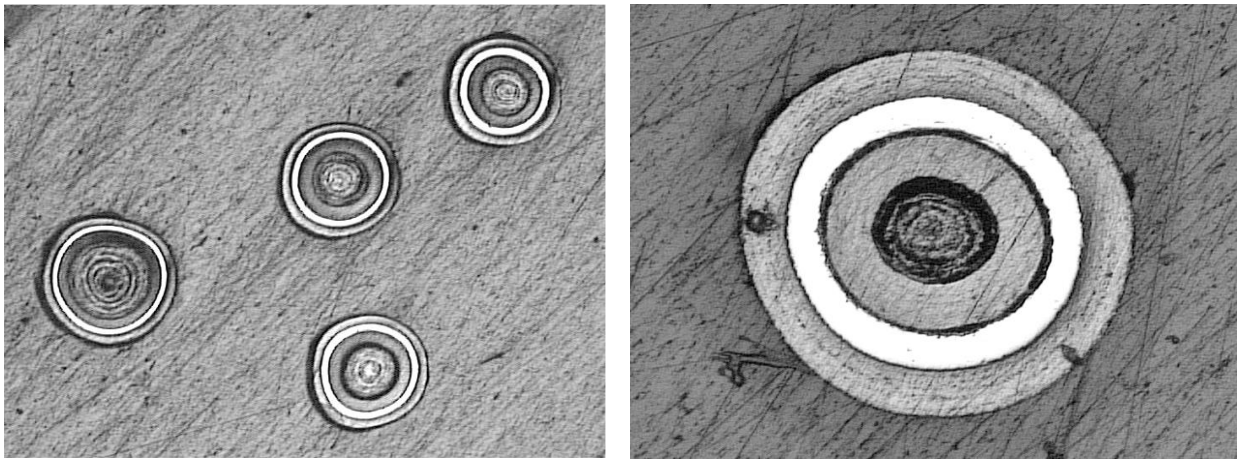

Figure 7: Sections of UC_2 coated particles.

The structure of the coated particle sections allows classifying them as TRISO particles, with a dense silicone carbide layer located between layers of pyrocarbon. At the places of the kernels, only hollows are visible on the sections presented due to the of low strength of the bonding between fuel kernel and porous pyrocarbon buffer layer, which led to a detachment of kernels during the polishing procedure.

The diameter of the kernels is very important for a successful isolation procedure. Therefore, several coated particles were cracked by point loading in a micrometer. The UC_2 fuel kernel diameter could be estimated with approximately 0.18 mm.

2.2 Isolation Technique by Milling

The kernels were isolated from the coatings by mechanical cracking using a Retsch milling machine (Figure 8) provided by the Retsch company (see http://www.retsch.com). Before isolation, the mill was calibrated and the distance between the work faces was adjusted to be slightly higher than the diameter of a UC_2 fuel kernel. Approximately 5 g of coated particles was treated at one run. All isolation steps were performed in argon-saturated deionised water in order to prevent dust formation and direct contact of the fuel kernels with air.

The mill was operated for approximately 15 minutes and then switched off. The content of the mill was rinsed by deionised water through a set of two subsequent sieves of 0.20 and 0.16 mm mesh size. The mesh size apertures were selected according to the kernels size of 0.18 mm. Thereafter, the content of the 0.16 mm sieve was placed in a Petri dish, and fuel kernels were separated from broken coatings by swivelling in water due to the floating behaviour of the kernels and coatings.

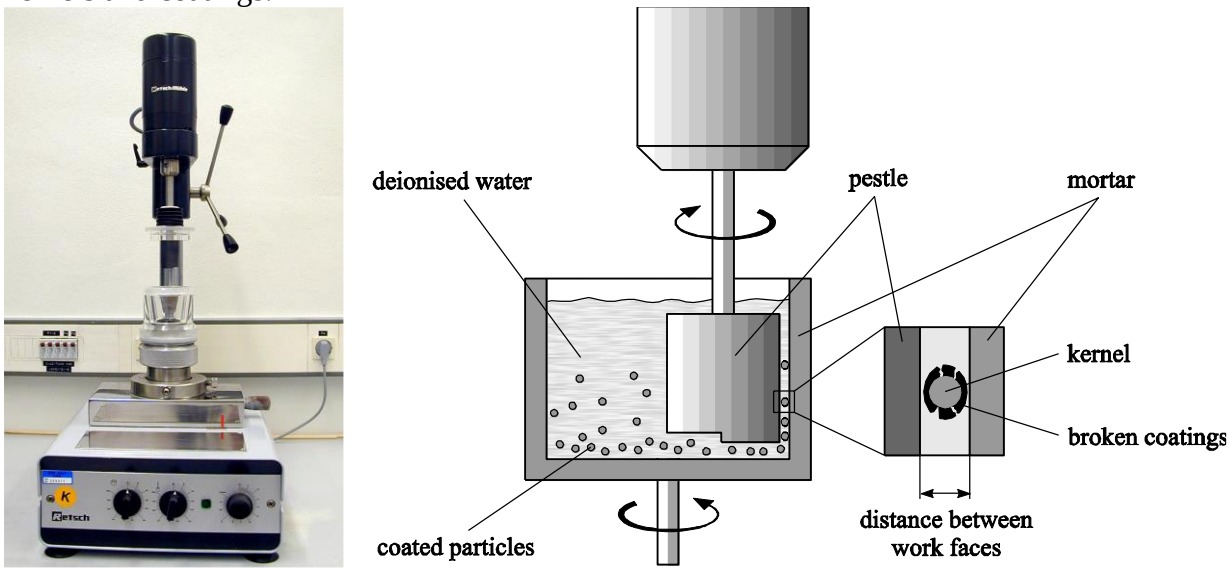

Figure 8: Isolation of fuel kernels from coated particles by means of a Retsch milling machine.

After drying a test sample of kernels was investigated be means of a scanning electron microscope (SEM). As can be seen in Figure 9, after isolation the kernels still bear a rest of their pyrocarbon buffer layer. To remove this surface contamination, the kernels were thoroughly cleaned in an ultrasonic bath for 90 minutes.

After ultrasonic cleaning the kernels were dried for 48 hours in a desiccator in vacuum and finally stored in argon atmosphere.

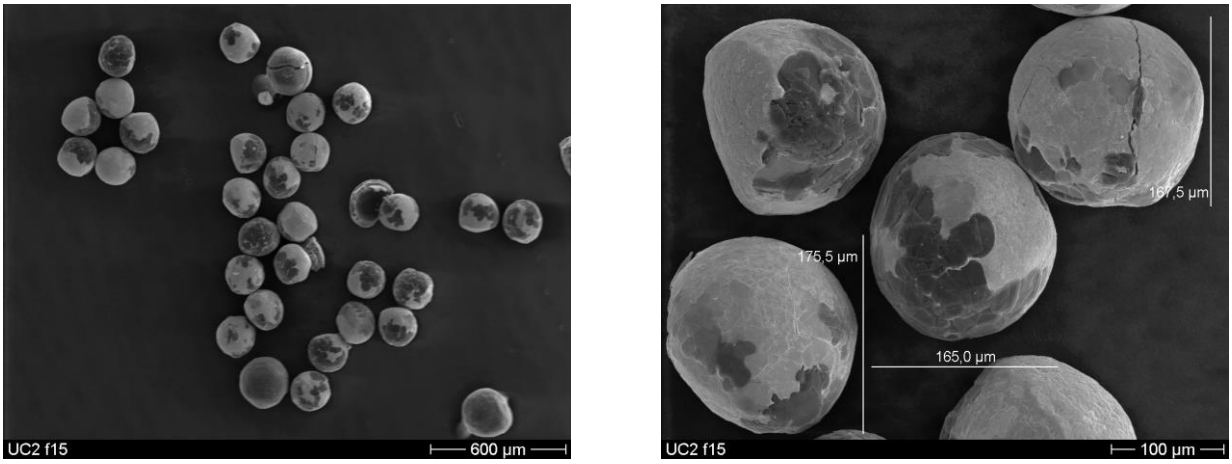

Figure 9: UC_2 kernels after isolation in a milling machine.

2.3 Characterisation of Isolated UC_2 Kernels

SEM investigations (Figure 11) show that isolated kernels have regular clean surfaces and are intact. A detailed photograph of a typical UC_2 fuel kernel surface is presented in Figure. The surface is facetted with a facet size of about 25 micrometer. This facet size is more likely connected with the fabrication procedure, rather than represents the grain size of the material. The kernel seems to have approximately reached its theoretical density.

XRD investigations (Figure12) show that the fuel kernels consist of only one crystal phase, i.e. tetragonal body-centred UC_2 with lattice parameters of a=0.352±0.001 and c=0.599±0.001 nm. The theoretical density is calculated with 11.75 g/cm^3.

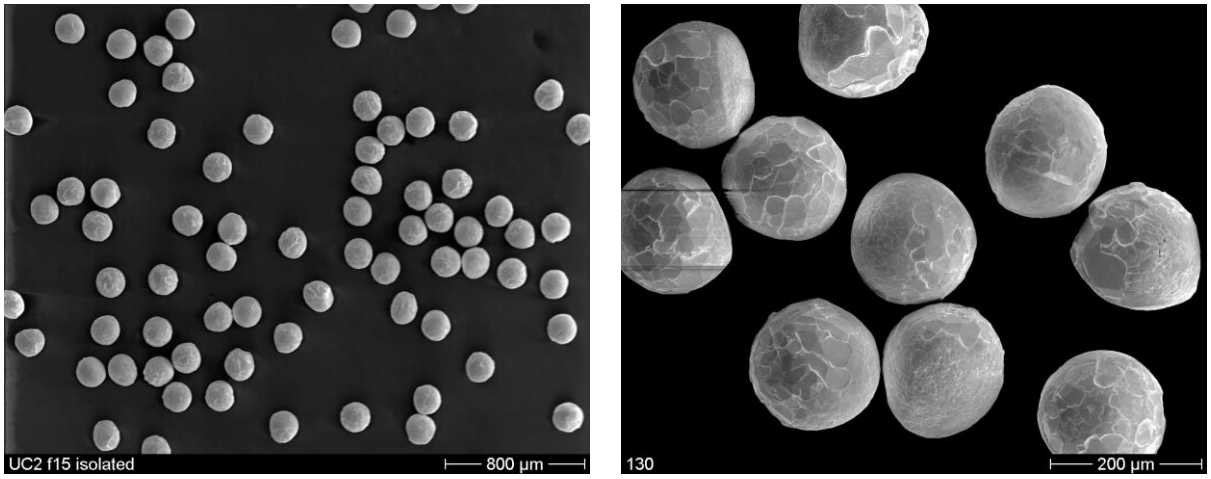

Figure 10: Isolated UC_2 kernels of final quality.

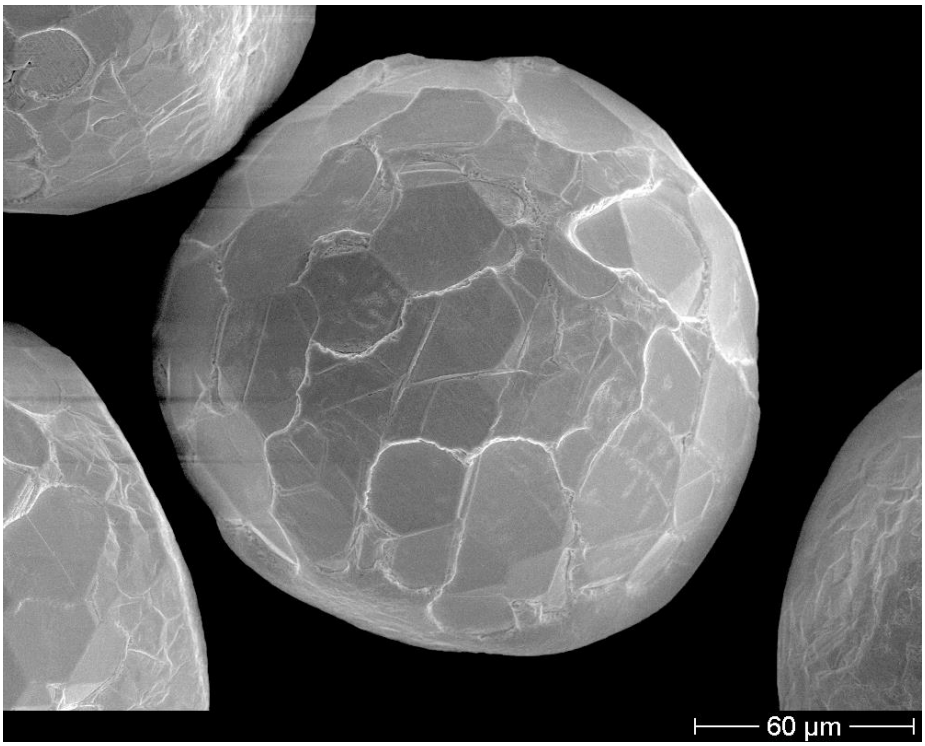

Figure 11: Surface of UC_2 fuel kernels.

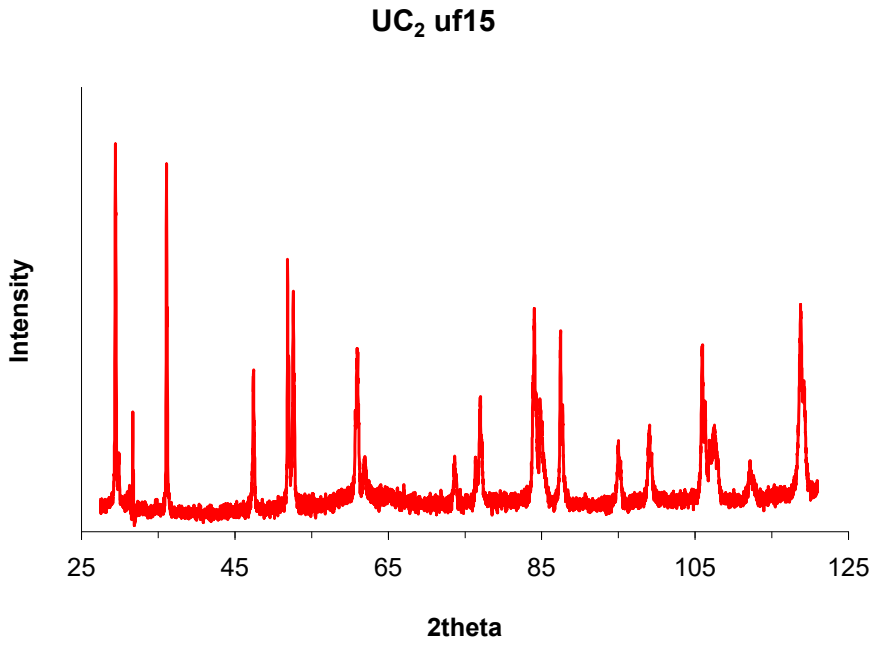

Figure 12: XRD spectra of a UC_2 fuel kernel.

2.4 Determination of Recovery Rate of Isolation Procedure

Before and after the isolation procedure the masses of initial coated particles and resulting kernels was determined. It could be derived, that from one gram of coated particles about 0.1 g of UC_2 fuel kernels can be obtained.

The second step was to determine the mass of single coated particles and fuel kernels. Since they are very small, approximately 500 particles and kernels were weighed on an analytical balance. The exact number of particles, taking part in the measurement, was then determined from macro-photographs. Based upon this procedure, the average weight was assessed to be 0.281 mg for a single coated particle and 0.044 mg for a UC_2 kernel, respectively. This means that the fuel kernel mass is only 15.7% from that mass of a coated particle.

Therefore, the recovery rate of the isolation procedure used can be estimated as 60%. It should be noted here, that the isolation procedure used was applied to obtain the best quality of the kernels, and no efforts were made to optimise the recovery rate of uranium because the purpose of these tests was to prepare samples for further leaching investigations and not to develop a segregation method with high throughput.

3 Conclusions

A comparison of the other processes shows the following benefits and draw-backs:

3.1 Diamond Disk Mill

Benefits
- High CP Throughput
- Fracture rates ~ 100%

Draw-Backs
- Difficult for Hot-Cell Operation (complex, high maintenance efforts)
- Sensible calibration of the milling gap
- Rather high fracture of kernels
- High fine dust generation
- No separation of kernels and coatings

3.2 Double-roll-crusher

Benefits
- High CP Throughput
- Fracture rates ~ 100%

Draw-Backs
- Difficult for Hot-Cell Operation (moving parts, maintenance)
- No separation of kernels and coatings

3.3 Pneumatical Methods

Benefits
- Suitable for Hot-Cell operation (no moving parts, low maintenance efforts)
- Milling and separation of kernels and coatings in one step
- Low fine dust generation
- Low kernel damage rate
- Continuous operation possible

Draw-Backs
- High gas throughputs
- High filter performance needed
- Relatively low CP throughput

3.4 Retsch Mill

By the Retsch Mill process (see http://www.retsch.com), UC_2 fuel kernels were successfully isolated from coatings by means of an automated procedure. The isolated kernels are intact, have no visible surface contaminations. The process is rather simple and effective but needs to be conducted under water and may produce secondary liquid waste. However, operation under a liquid prevents release of dust. Ultrasonic treatment can be used to remove residua of coating on the kernels.

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