# Immobilization in Cement of Rice Husk used as Biosorbent of Radionuclides Present in Radioactive Liquid Waste – 17225

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# ABSTRACT

The use of new techniques for the treatment of radioactive liquid wastes has been studied in the last few years by many countries. In this context, the biosorption has been an attractive process. In Brazil the Radioactive Waste Management Laboratory of Nuclear and Energy Research Institute (IPEN-CNEN/SP), studied some biomasses to be used as biosorbents to remove radionuclides of the radioactive liquid waste stored in this institute. The rice husk is a low cost and wide available byproduct of the agriculture and its biosorption capacity has been proved as feasible. Thus, it is necessary to evaluate if its immobilization in a cementitious matrix will result in a waste form that meets the requirements of Brazilian regulations for final disposal of low and intermediate level waste. This work aimed at evaluating the properties of the waste form with incorporated rice husk were evaluated, as free water, workability, setting time and mechanical strength. The results indicated that cement matrices with 5 and 10% of biomass and water/cement ratio of 0.30 and 0.35 are viable for the production of waste forms that meets the Brazilian regulations.

## INTRODUCTION

The use of new techniques for the treatment of liquid radioactive wastes has been studied in the last few years by many countries. In this context, the biosorption has been an attractive process. It uses vegetable solid materials or microorganisms for retention, removal or recovery of heavy metals in a liquid environment [1-5].

The Radioactive Waste Management Laboratory of Nuclear and Energy Research Institute (IPEN-CNEN/SP), Sao Paulo, Brazil, studied some biomasses to be used as biosorbents to remove radionuclides of the radioactive liquid waste stored in this institute. One of the biomasses studied was the rice husk because of its low cost and wide availability in Brazil [6-8].

Rice husk presents biosorption capacity that can be improved modifying its structure by chemical treatments. Assays conducted with this biomass showed good capacity to retain radionuclides in radioactive liquid waste (both modified and raw rice husk) [9].

After the biosorption process, the biomass becomes a radioactive waste, while the liquid can be processed as common waste. The Brazilian regulations require that the biomass must be immobilized in a cementitious matrix in order to prepare waste packages for the final deposition [10].

Although the biosorption has been shown feasible for the treatment of radioactive liquid waste, it is necessary to evaluate if the immobilization of the biomass in a cementitious matrix will result in a waste form that meets the requirements of Brazilian regulations for final disposal of low and intermediate level waste [11].

Thus, this work aims at evaluating the immobilization of rice husk in a cementitious matrix. The properties of the waste form needs to meet the requirements of Brazilian regulations.

## METHODS

The biosorption capacity of raw and activated rice husk was evaluated, using rice husk obtained by a local producer, activated and sieved before the biosorption process, as described by Ferreira et al [9]. The rice husk was activated, i.e. chemically modified, treating it with 0.5 M HNO<sub>3</sub> and 0.5 M NaOH solutions.

As result of the activation process, the HNO<sub>3</sub>/NaOH solutions were able to remove surface impurities on the activated form, decrease the real density, apparent density, and surface area values and improving the biosorption of Am-241, Cs-137 and Uranium (detailed results in reference [9]). The biomasses were dried before the immobilization in a cement matrix.

Fig. 1 presents the micrograph images of rice husk before and after activation by scanning electron microscopy. In Fig. 1, it is possible to see that  $HNO_3/NaOH$  solutions were able to remove surface materials on the activated form.

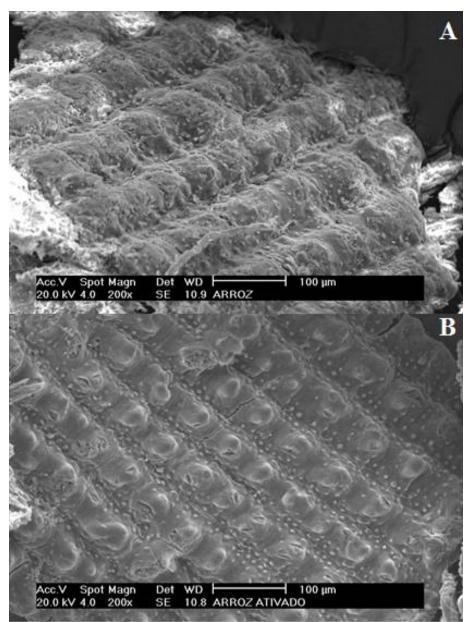


Fig. 1. Scanning electron microscopy of rice husk A (raw husk), B (activated husk).

Cylindrical cement paste specimens containing the rice husk were cast in the laboratory varying the water/cement ratio (0.30, 0.35 and 0.40) and the biomass content (5, 10, 15, 20 and 25%). The cement used was Ordinary Portland Cement and no additives or admixtures were used.

The mixture was done adding the cement to the biomass and water and mixing in a mechanical mixer. The mixture was maintained under stirring until obtaining a homogeneous paste, and transferred to the moulds in three layers.

The specimens were then submitted to tests of workability, setting time, drainable

water and mechanical strength. The free water content was determined after 24 hours of the beginning of cure. If a sample contains free water more than 0.5% of total volume, the waste form is be accepted for final deposition. So this parameter excludes a mixing formula.

The workability was tested by Marsh funnel and mini-slump cone tests. The setting time was determined with Vicat's apparatus. The Fig. 2 shows the apparatus used in each test. The mechanical strength was determined in axial compression equipment after 28 days of cure.



Fig. 2. Marsh's funnel, Vicat apparatus and mini slump cone tests

# **RESULTS AND DISCUSSION**

The results of free water content are showed in Table 1. As it is an exclusion parameter, the samples with 20 and 25% of raw rice husk and with 15, 20 and 25% of activated rice husk incorporated to the matrix were discarded, as they showed free water.

| Water/Cement | Biomass % | Raw Rid | ce Husk | Activated Rice Husk |    |
|--------------|-----------|---------|---------|---------------------|----|
| Ratio        |           | Yes     | No      | Yes                 | No |
|              | 5         |         | Х       |                     | Х  |
|              | 10        |         | Х       |                     | Х  |
| 0.3          | 15        |         | Х       | X                   |    |
|              | 20        | Х       |         | X                   |    |
|              | 25        | Х       |         | X                   |    |
|              | 5         |         | Х       |                     | Х  |
|              | 10        |         | Х       |                     | Х  |
| 0.35         | 15        |         | Х       | X                   |    |
|              | 20        | Х       |         | X                   |    |
|              | 25        | Х       |         | X                   |    |
| 0.4          | 5         |         | Х       |                     | Х  |
|              | 10        |         | Х       |                     | Х  |
|              | 15        |         | Х       | X                   |    |
|              | 20        | Х       |         | х                   |    |
|              | 25        | Х       |         | Х                   |    |

TABLE 1. Free water content results.

In the Marsh Funnel test, some mixtures present no flow, since the biomass cause the blockage of the funnel. Thus, the mini slump test was done in all samples. The results obtained are showed in Table 2. The presence of the biomasses results in an increase of workability in all cases. As expected, increasing the biomass content and the cement/water ratio the workability was increased as well.

| TABLE 2. Workdomity results by Marsh Further and Miner burnp tests. |                 |                        |                           |                 |                     |                           |       |
|---|-----------------|------------------------|---------------------------|-----------------|---------------------|---------------------------|-------|
| Water/ <sub>E</sub> .   |                 | Marsh Funnel (minutes) |                           |                 | Mini Slump (mm)     |                           |       |
| Ratio   | Cement<br>Paste | Raw<br>Rice<br>Husk    | Activated<br>Rice<br>Husk | Cement<br>Paste | Raw<br>Rice<br>Husk | Activated<br>Rice<br>Husk |       |
|   | 0               | No flow                | -                         | -               | 36.68               | -                         | -     |
| 0.3   | 5               | -                      | No Flow                   | No flow         | -                   | 54.93                     | 51.71 |
|   | 10              | -                      | 4                         | 1.23            | -                   | 57.09                     | 78.61 |
|   | 0               | 5.5                    | -                         | -               | 47.60               | -                         | -     |
| 0.35  | 5               | -                      | 2.5                       | 1.21            | -                   | 67.43                     | 73.53 |
|   | 10              | -                      | 1                         | 0.38            | -                   | 71.37                     | 94.90 |
|   | 0               | 1.5                    | -                         | -               | 62.31               | -                         | -     |
| 0.4   | 5               | -                      | 0.5                       | 0.41            | -                   | 95.76                     | 89.20 |
|   | 10              | -                      | 0.33                      | 0.28            | -                   | 110.56                    | 93.53 |

TABLE 2. Workability results by Marsh Funnel and Mini Slump tests.

Results of initial and final setting time are presented in Table 3. The Vicat's Apparatus was used to assess these values. The presence of biomass did not inhibit the setting of the mixtures, but increase the setting time significantly.

| Water/<br>Cement Biomass % |    | Cement Paste |           | Raw<br>Rice Husk |           | Activated<br>Rice Husk |           |
|----------------------------|----|--------------|-----------|------------------|-----------|------------------------|-----------|
| Ratio                      |    | Initial (h)  | Final (h) | Initial (h)      | Final (h) | Initial (h)            | Final (h) |
|                            | 0  | 3,78         | 5,03      | -                | -         | -                      | -         |
| 0.3                        | 5  | -            | -         | 4.00             | 7.25      | 6.00                   | 8.30      |
|                            | 10 | -            | -         | 5.50             | 9.25      | 7.50                   | 11.25     |
|                            | 0  | 4,66         | 6,91      | -                | -         | -                      | -         |
| 0.35                       | 5  | -            | -         | 5.94             | 8.50      | 7.94                   | 10.50     |
|                            | 10 | -            | -         | 7.94             | 10.50     | 8.94                   | 12.00     |
|                            | 0  | 4,66         | 8         | -                | -         | -                      | -         |
| 0.4                        | 5  | -            | -         | 5.94             | 9.50      | 9.94                   | 11.50     |
|                            | 10 | -            | -         | 8.94             | 12.50     | 11.94                  | 14.50     |

TABLE 3. Initial and Final setting time results, assessed by Vicat's Apparatus.

The results of mechanical strength are showed in Table 4. In comparison with the cement paste, the presence of the biomasses decreases the mechanical strength of the samples in general. The exception was the samples with activated rice husk and cement/water ratio of 0.40.

The Brazilian regulations indicate a minimum of 10 MPa of mechanical resistance. All specimens tested were above this limit, except the one with W/C ratio of 0.40 and 10% of rice husk.

|        | <u> </u>    |                |                      |                |  |  |
|--------|-------------|----------------|----------------------|----------------|--|--|
| Water/ | Biomass     | Cement Raw     |                      | Activated      |  |  |
| Cement | ыотазз<br>% | Paste          | Rice Husk            | Rice Husk      |  |  |
| Ratio  | 70          | MPa            | ± Standard Deviation |                |  |  |
|        | 0           | $48.0 \pm 3.5$ | -                    | -              |  |  |
| 0.30   | 5           | -              | $19.5 \pm 2.9$       | $40.1 \pm 1.5$ |  |  |
|        | 10          | -              | $18.5 \pm 1.5$       | 29.3 ± 2.1     |  |  |
|        | 0           | $43.9 \pm 2.8$ | -                    | -              |  |  |
| 0.35   | 5           | -              | $20.2 \pm 1.1$       | $33.3 \pm 3.0$ |  |  |
|        | 10          | -              | $15.7 \pm 0.5$       | $28.7 \pm 0.5$ |  |  |
|        | 0           | 23.7 ± 1.8     | -                    | -              |  |  |
| 0.40   | 5           | -              | 15.1 ± 1.8           | $32.4 \pm 0.6$ |  |  |
|        | 10          | -              | 7.1 ± 1.0            | $29.0 \pm 0.9$ |  |  |
|        |             |                |                      |                |  |  |

TABLE 4. Mechanical Strength results in MPa.

### CONCLUSIONS

The results obtained indicate that in comparison with pure cement paste, the presence of the biomasses in the cement matrix increase the viscosity and the initial and final setting time. The mechanical strength was below in biomasses matrix, but still above the limit of the Brazilian regulations of 10 MPa.

The results indicate that cement matrices with 5 and 10% of biomass and water/cement ratio of 0.30 and 0.35 are viable for the production of waste forms that meets the Brazilian regulations.

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