THE Ca BINDING TO THE HULL OF *NIXTAMALIZED* CORN GRAINS AS DETECTED BY ^{57}FE MÖSSBAUER SPECTROSCOPY AND RELATED TECHNIQUES

E. Reguera[1], H. Yee-Madeira[2,], R. Gonzalez[3], F. Sánchez-Sinencio[4]*

[1]Institute of Materials and Reagents, Havana University, Havana, Cuba
[2] Depto. Física, Esc. Sup. Física y Matemáticas-IPN, Av. IPN s/n, Edif . 9, U. Prof. "ALM"
Col. Lindavista, 07738, México, D.F., México
[3] Faculty of Chemistry, Havana University, Havana, Cuba
[4] Departments of Physics, CINVESTAV-IPN, Mexico, D.F.

Abstract. Tortilla and other products elaborated from *nixtamalized* (alkaline cooking in a saturated solution of $Ca(OH)_2$) corn grains are the main source of Ca intake in Mexico, mainly in rural regions. In that cooking process Ca is mainly retained in the germ and the corn hull. In the germ Ca appears as salts of fatty acids. According to IR and ^{13}C CP/MAS NMR data, the hull binds Ca through the hemicelluloses acidic species (uronic acids). Mössbauer spectra of *nixtamalized* hull samples, where Ca^{2+} was substituted by $^{57}Fe^{2+}$, suggest the existence of two slightly different sites for Ca in the corn hull.

1. Introduction

In Mexico corn is consumed mainly as Tortillas. Tortillas are prepared from mass or flours obtained through an alkaline cooking and steeping of corn grains in a saturated solution of $Ca(OH)_2$, process that is used from prehispanic times. The alkaline treatment makes corn proteins available and incorporates Ca to the cooked grains, increasing the nutritional levels of the mass or flours elaborated with *nixtamalized* corn [1]. Approximately a 50% of Ca intake in Mexico, mainly in rural regions, is provided by Tortilla and other products elaborated from *nixtamalized* corn [2]. It is accepted that of the total Ca employed in *nixtamalization* only a small fraction is retained in the grain during the cooking and resting periods [3]. In the germ Ca is found as salts of fatty acids, due to a partial saponofication of its fats during the alkaline cooking, while in endosperm it is forming inclusion compounds of these salts within the amylose helical structure [3]. Little attention has been given to the possible retention of Ca by the corn hull (pericarp) and on its state in this part of the grain, although, as will be discussed later, the presence there of species capable of bind Ca. In this contribution we are reporting a study on the state of Ca in the hull of *nixtamalized* corn grains, using infrared (IR), ^{57}Fe Mössbauer, ^{13}C cross polarization magic angle spinning NMR (^{13}C CP/MAS NMR) and X-ray energy-dispersed spectroscopy (EDS) as sensing techniques.

2. Experimental

Samples of the different parts of the corn grain before and after their alkaline cooking for 30 min. at 85 ºC in a saturated solution of $Ca(OH)_2$ were studied. Additionally, samples of the corn hull previously separated from the grain with and without the alkaline treatment were also analyzed.

The IR spectra were run in KBr pressed disks using an FTIR spectrophotometer (from Bruker). The ^{13}C CP/MAS NMR spectra were recorded in a Bruker ASX300 (300 MHz) spectrometer.

The Mössbauer spectra of *nixtamalized* hull were obtained from samples in which part of Ca^{2+} was substituted by $^{57}Fe^{2+}$. The spectra were recorded at room temperature with a ^{57}Co/Rh source using a constant acceleration spectrometer (from Wissel) and then fitted with a least-squares minimization algorithm in order to obtain the values of isomer shift (δ), quadrupole splitting (Δ), line width (Γ) and relative area (A). The values of δ are reported relative to sodium nitroprusside.

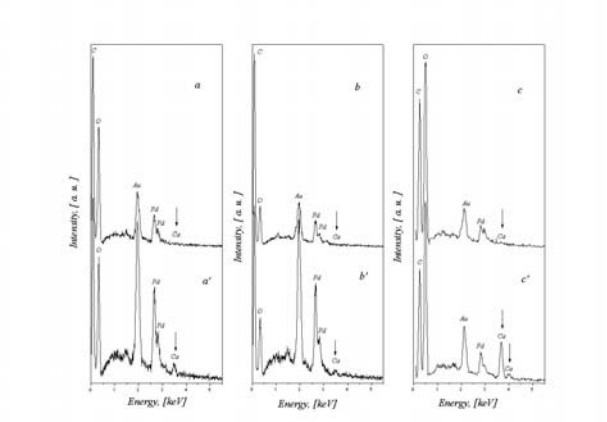

Figure 1. EDS spectra of different parts of the corn grain before (*a,b,c*) and after (*a´,b´,c´*) its alkaline cooking (nixtamalization). (*a,a´*): Germ; (*b, b´*): Endosperm; (*c,c´*): Hull. Observe that Ca is mainly retained in the hull.

* Corresponding author E-mail: yee@esfm.ipn.mx and COFAA-Fellow