International Journal of Earth, Energy and Environmental Sciences
ISSN: 2517-942X
Vol:10, No:10, 2016

Optimal Consume of NaOH in Starches Gelatinization for Froth Flotation

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***Abstract*—**Starches are widely used as depressant in froth flotation operations in Brazil due to their efficiency, increasing the selectivity in the inverse flotation of quartz depressing iron ore. Starches market have been growing and improving in recent years, leading to better products attending the requirements of the mineral industry. The major source of starch used for iron ore is corn starch, which needs to be gelatinized with sodium hydroxide (NaOH) prior to use. This stage has a direct impact on industrials costs, once the lowest consumption of NaOH in gelatinization provides better control of the pH in the froth flotation and reduces the amount of electrolytes present in the pulp. In order to evaluate the gelatinization degree of different starches and flour were subjected to the addiction of NaOH and temperature variation experiments. Samples of starch (corn, cassava, HIPIX 100, HIPIX 101 and HIPIX 102 commercialized by Ingredion) and flour (cassava and potato) were tested. The starch samples were characterized through Scanning Electronic Microscopy and the amylose content were determined through spectrometry, swelling and solubility tests. The gelatinization was carried out through titration with NaOH, keeping the solution temperature constant at 40 ^{o}C. At the end of the tests, the optimal amount of NaOH consumed to gelatinize the starch or flour from different botanical sources was established and a correlation between the content of amylopectin in the starch and the starch/NaOH ratio needed for its gelatinization.

***Keywords*—**Froth flotation, gelatinization, sodium hydroxide, starches and flours.

I. Introduction

THE froth flotation routes of iron can be classified in two groups, direct or inverse flotation. Another classification, regarding the type of collector used divides the process in four groups, cationic or anionic iron oxide flotation, and cationic or anionic quartz froth flotation. In any froth flotation process the hydrophobic particles are carried out from pulp to froth zone by means of true flotation, but undesirable gangue minerals also report to the concentrate through hydraulic entrainment and entrapment rather than true flotation [1].

Nowadays, the inverse cationic route for iron ore flotation is, by far, the most widely adopted method in Brazil. Amines and diamines are used as collectors and starch (or amylum), after gelatinization with NaOH, as depressants. Frothers are not used because the collector acts as one [20], [21].

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Corn starch is the default depressant for iron ore since 1978 [2]. Modified corn starches are composed by amylopectin (70-80%) and amylose (20-30%) without impurities such as fibers, mineral matter, oils and proteins normally present in conventional starches [2]. Zein, a class of prolamine protein present in corn, presents a depressant action towards hematite. Despite practical industrial evidence that both types of starch (modified or conventional) yielded similar performance, suppliers of conventional starch claim that proteins content in starch might be harmful to flotation results. Experimental results from microflotation tests in modified Hallimond tube showed that zein has depressant properties for hematite as efficient as amylopectin and conventional corn starch [3]. The authors point out that oil (triglycerides) present in conventional starch act as an antifoam agent spoiling the flotation process if its content exceeds 1.8%. The starch's depressant action is due to the coating of a natural low energy hydrophobic mineral surface with a hydrophilic film to prevent the attachment of air bubbles [4].

Starch simplified formula is $(C_6H_{10}O_5)_n$, where n represents aldohexose units (a monosaccharide). The polymerization index n, and consequently the starch molecular weight varies in a wide range, as well as the ratio between the larger and nonlinear amylopectin macromolecules and the smaller and linear amylose [5]. In the starch polymer, only three hydroxyl groups of the cyclic glucose units are free and may rotate to one side of the molecule ring, making that side more hydrophilic. The opposite side is consequently slightly hydrophobic due to the exposed – CH groups. In fact, in aqueous solutions amylose forms a helix with six glucose monomers per turn. The interior of the helix is hydrophobic, whereas the outer shell is hydrophilic [6].

Amylose and amylopectin molecules are connected to each other via hydrogen bonds in the starch molecules, forming granules ranging from 3 μm to 100 μm length that are insoluble in cold water. The amylopectin is a branched molecule consisting of several thousand of cross-linked short amylose chains, with normal chain of glucose units joined by α -1,4-linkages, side chains joined to the main chain by α -1,6-glucosidic bonds and molecular weight varying from 10 to 100 times the amylose weight [3]. The side chains could have other side chains (or branches), resulting in a branched polymer molecule [7]. Amylopectin is also easily dispersed in water and shows a lower tendency to form gel and to retrogradation, which is a reaction that takes place when the amylose and amylopectin chains in gelatinized starch realign themselves as the gelatinized starch cools down [5]. On the other hand, amylose is a linear, flexible chained molecule displaying random coil behavior in aqueous alkali solution [8]. It consists of long chains of D-glucose units joined by α-1,4-glucosidic bonds. The average molecular weight of amylose is 0.31 x 10^6 and for amylopectin is 1,500 x 10^6 for corn starch, by measured by light scattering [8]. The amylopectin component of starch takes part in flotation and flocculation, but the amylose is unable to react with any mineral surface. Studies indicate that starch adsorption onto hematite surface are due to the availability of higher concentrations of hydroxylated sites in the metal [9].

Studies showing the importance of the amylose/amylopectin ratio in starch during hematite depression, point out that amylopectin reduces the hematite froth flotation more profoundly than amylose when a primary ether amine is used as a collector [3]. This ratio is measured through potentiometric iodine titrations and spectrophotometric analysis [5] and is different for starch-containing vegetables, or even for distinct varieties of the same vegetable. Nevertheless, better results were achieved when using starch with a 75/25% ratio instead of pure amylopectin [3].

All types of large molecular weight non-modified starches must be put into solution in a process known as gelatinization prior to its use as a depressant. The process consists in heating a starch suspension in water above 56 °C weakening the intergranular hydrogen bonds and causing swelling of the granules, loss of birefringence, increase of the clarity and viscosity of the solution [3]. The gelatinization should not use grains coarser than 1 mm to avoid difficulties in solubilization and can be performed by means of warm water or by addition of NaOH (called alkali gelatinization) at room temperature, with the latter being the method adopted in the mineral industry. However, higher NaOH concentrations induces two changes that have conflict effects on the settling behavior of the hematite. On one hand, it generates acidic groups on the starch, which may promote starch adsorption on the hematite and improve flocculation and settling (referred as bridging). On the other hand, higher concentrations could lead to starch chain breakdown, lowering its flocculation power [10]. The alkali gelatinization involves a disruption of the starch granule integrity and a loss in its crystallinity. Drying may result in the partial recrystallization, but the original integrity of the starch granule is not regained [11].

The effectiveness of the alkali gelatinization is strongly affected by the starch/NaOH ratio used in the gelatinization [12] and the dissolution technique [13], being the typical ratio 5:1 [4], [14]. Some studies suggest that the starch solution was designed to yield a maximum concentration of 0.1% w/w and must be prepared daily to avoid the retrogradation [15], [16]. However, this is not well stablished and other studies disagree with using concentrations up to 3% [17].

The temperature needed for gelatinization decreases with increasing of the amylopectin content. Retrogradation occurs spontaneously when starch solutions are stored at low temperatures at neutral pH. Amylose's retrogradation may occur within a period of four to five hours after the gelatinization, while the amylopectin retrogrades only 10% within 100 days [5].

The primary adsorption mechanisms of starch on hematite were proposed as non-selective hydrogen bonding and electrostatic forces, mainly because of the presence of a large number of hydroxyl groups in starch molecules and on hematite surface. As confirmed by several studies, starch adsorbs more on hematite surface than on quartz [18]. The adsorption density of starch on quartz surface is approximately 10 times less than that on hematite [19]. At pH above eight, the starch adsorption is almost nonexistent on non-activated quartz surface, while it is noticeable on hematite surface. The reasons for this selectivity are a better ability of hematite surface to form hydrogen bonds with the depressant and the fact that quartz surface is more negative than hematite, being the macromolecules slightly negative because of OH- adsorption [3]. On the other hand, the starch adsorption on hematite increases as the pH value decrease [15].

Other vegetable species, such as cassava, potato, wheat, rice, arrowroot, can produce starch with potential to be used in flotation. The most attractive among them, considering the cost of production, is cassava, which grows widely in warm weather countries, with no need of fertilizers or soil correction. The major obstacle to its use is the absence of major suppliers. The starch fraction content (amylopectin + amylose) extracted from cassava is higher than in corn because proteins and oil contents are lower in cassava, which prevents the risk of froth suppression. Cassava starch shows higher viscosities than corn starch, an indication of higher molecular weight, which can lead to more effective depressant action [14]. Potato flour has been used industrially in Europe, but there are no records of its use in the mining industry so far, mainly due the fact that potato degrades much faster than corn and have a high price [6].

II. Methodology

Samples of starch (corn and cassava) and flour (cassava and potato), donated by Cargill, and corn starch with commercial name HIPIX 100, HIPIX 101 and HIPIX 102, donated by Ingredion, were used in the tests. The first stage aimed to characterize the starches in order to better understand their gelatinization. To determine the amylose content a method proposed by the American Association of Cereal Chemists (AACC) number 1995 was used, which is a simple colorimetric procedure. Samples of starch were added to a solution of 1 mL of acetic acid at 1 $mol.L^{-1}$ and 2 mL of solution of iodine-potassium iodide, which reacts with starch to form a blue colored complex. This complex is developed due to the imprisonment of iodine inside the chain of amylose. The solution was then stored for 30 minutes in a dark room and then using a spectrophotometer Biospectro, model SP220 read the absorbance at 620 nm. The content of amylose was calculated using the absorbance values read and a calibration curve made with pure amylose (supplied by Sigma-Aldrich) in the range of 0.004 $mg.mL^{-1}$ and 0.024 $mg.mL^{-1}$ (for this curve the obtained fit was r^2=0.998). The results were expressed in $mg.ml^{-1}$ and performed in triplicate.

Starch swelling power and solubility were also measured to calculate the amylose content in the starch samples. When starch molecules are heated in water, the crystalline structure is broken and the water molecules form hydrogen bonds between amylose and amylopectin, exposing its hydroxyl groups. This causes an increase in the granule size (a swelling) and in its solubility [22]. This swelling power and solubility varies according to the starch source, providing evidence of the interaction between the starch chains within the amorphous and crystalline domains. The extension of these interactions is influenced by the ratio amylose/amylopectin due to molecular features distributed, molecular weight, degree, length of branches [23]. The swelling power was obtained by the relation between the final mass swelled and the starch initial mass. The starch solubility was calculated by the relation between the soluble mass and initial amount of starch (expressed in percentage).

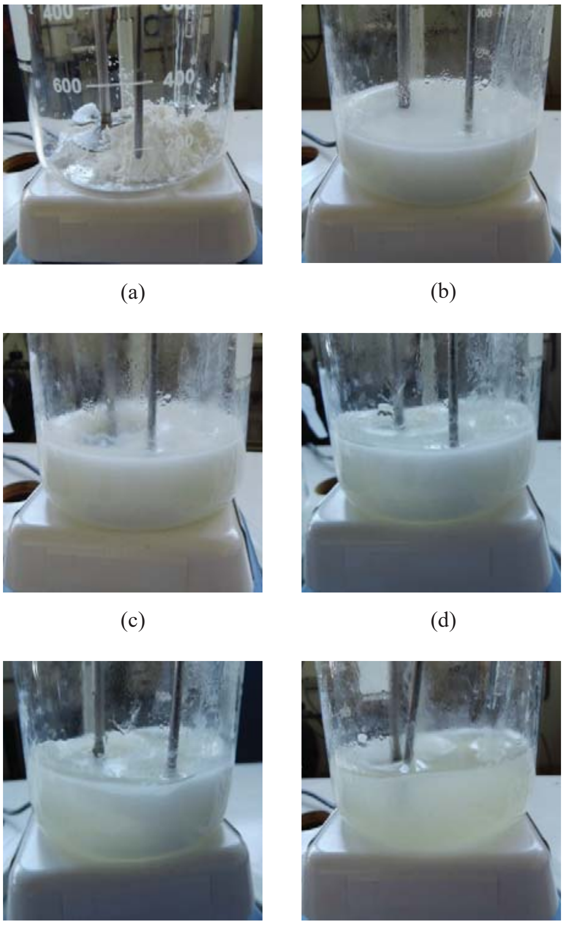

Fig. 1 Six steps in the starches and flours alkaline gelatinization process (a) starch sample, (b) starch solution after complete solubilization, (c), (d) and (e) steps in the titration process and (f) complete gelatinization of the sample

The second stage of methodology aimed to standardizing the ideal starch/NaOH ratio, avoiding the excessive use of NaOH. Starch and flour samples 20 g were placed in a 600 mL beaker on top of a heating plate Ika C MAG HS 4. Then 200 mL of distilled water at 40 °C were added to the sample and the solution was kept under agitation at 1,200 RPM using a mechanical stirrer Fisatom 712 to promote a complete dilution of the starch sample. A pH meter Hanna Instruments HI2221 was installed in order to read the solution pH and temperature. After the complete dilution of the starch sample, the initial pH value was noted and the titration started. An aliquot of 1 mL of 10% NaOH solution was added every two minutes to the starch solution. Before a new addition of the NaOH solution, the pH was noted. The process was repeated until the point that the starch solution presented itself viscous and more transparent (also known as the turning point of the gelatinization). Six steps of the process can be seen in Fig. 1. All titration process was performed in triplicate keeping the temperature constant at 40 ºC.

III. Results and Discussions

A. Amylase Determination

Fig. 2 shows the amylase content measured by the of AACC 1995 method. The amylopectin content was evaluated by exclusion. The values obtained are similar to those available in the literature. The modified corn starch HIPIX 101, as expected, has approximately 82% of amylopectin, value much more significant than natural corn starch, which has only 28%. However other modified corn starches, such as HIPIX 100 HIPIX 102, showed a lower amylopectin content which can indicate that these starch come from a different corn specie than HIPIX 101.

B. Solubility and Swelling Tests

Fig. 3 shows the results of the swelling test for starches and flours tested. It is possible to note that the samples do not follow a specific trend. By contrast, Fig. 4 shows the contradiction between the real influences of the amylose/amylopectin ratio in the starches and flours solubility. It is possible to notice that cassava flour has the lowest swelling power and has the higher solubility. Similar behavior was observed by the potato flour. However, corn starches (modified or not) showed a different behavior.

C. Gelatinization Tests

It is well known that the higher is the percentage of amylopectin the lower is the temperature for the gelatinization [5]. Since the temperature was kept constant at 40 ºC the only variation was regarding the NaOH consumed in the process. The influence of the amylopectin ratio in the gelatinization is observed in Fig. 5, where it is possible to notice that HIPIX 100 achieved the complete gelatinization in the lowest pH (around 11.5) while the others samples did the same at a higher pH (around 12.5).

Table I summarizes the found results regarding the turning point (or gelatinization point) for the starches and flours tested. The Amylose / amylopectin ratio measured is presented, as well as the initial and final solution's pH. Cassava flour, which has the higher amylose / amylopectin ratio (1/0.62) consumed the higher volume of NaOH (13.7). In contrast, potato flour has the lower ratio (1/6.11) and consumed the higher volume of NaOH (5.3), as expected. This behavior was not seen with the modified starches (HIPIX 100, 101 and 102).

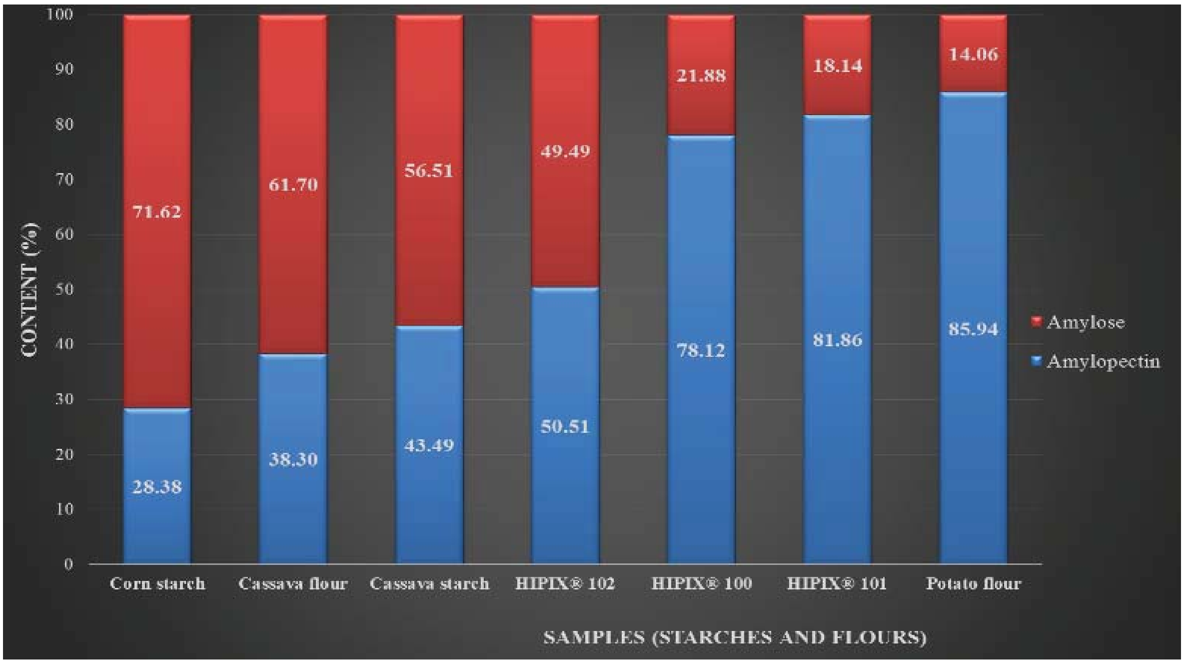

Fig. 2 Amylose and amylopectin contents in starches and flours tested

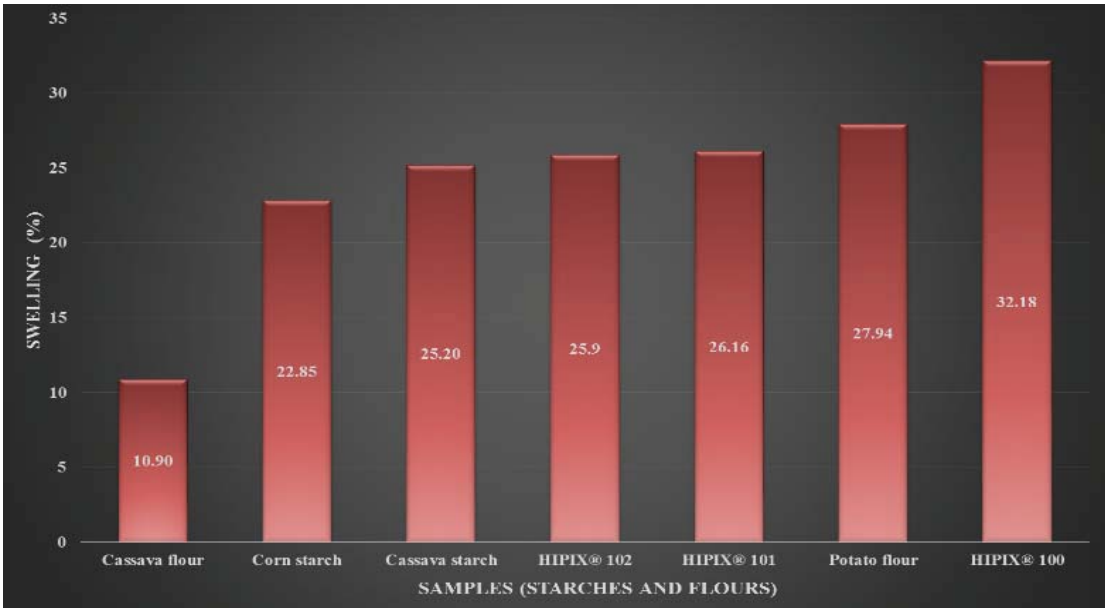

Fig. 3 Swelling test results for starches and flours tested

The addition of NaOH after the gelatinization of the sample did not increase the solution pH, as would be expected. Instead, a plateau was observed for all samples. An analysis of this result allowed the establishment of the minimum amount of NaOH needed to perform the complete gelatinization of the sample as presented in Table II. Potato flour showed the higher starch/NaOH ratio (35.7/1). Since this sample has the higher amylopectin content, this result agrees with the expected regarding the temperature need for the gelatinization. The same behavior can be seen for corn starch, which shows the least starch/NaOH ratio (13.3/1) and amylopectin content.

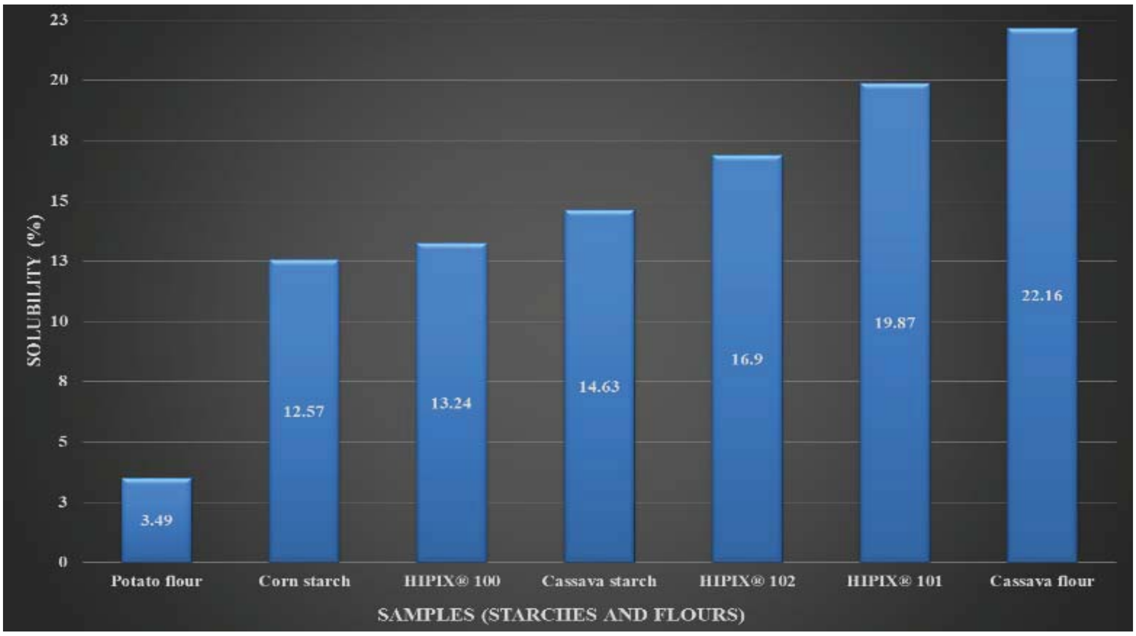

Fig. 4 Solubility test results for starches and flours tested

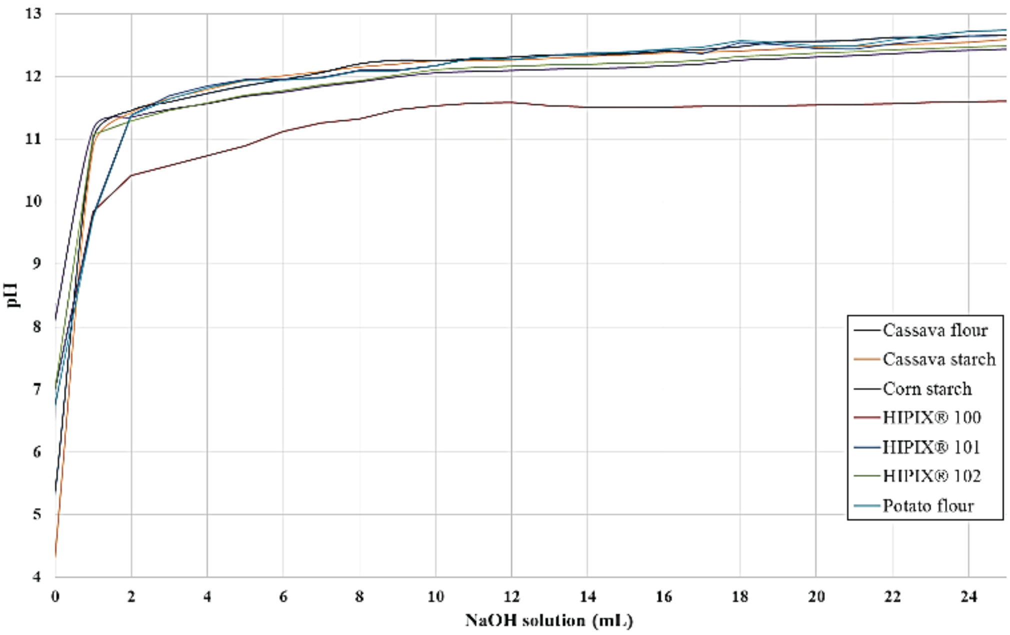

Fig. 5 Variation of the solution pH during the gelatinization tests at 40 ^{o}C with the NaOH addition

IV. Conclusions

The titration with NaOH in the complex solution starch/NaOH presented as an interesting tool for analysis of the gelatinization point of starches and flours. The presence of not broken or swollen granules varies with the ratio of starch/NaOH and reaction time. However, the understanding of NaOH consumption in water/starch solutions is critical, once it can have a successful gelatinization with lower amounts of NaOH, as shown in the tests.

The starch acts in the selectivity of the flotation process that is influenced by the state of liberation from the chains of amylose and amylopectin. The found results showed that mineral industry in Brazil are adopting starch/NaOH ratios varying from three to five times higher than necessary.

Another conclusion is that the higher the percentage of amylopectin, the lower the temperature and the lower starch/NaOH ratio for gelatinization.

TABLE I
DATA FROM GELATINIZATION TESTS

Starches and flours	Amylose / amylopectin ratio	Initial pH	Final pH	Average NaOH consumed (mL)
Cassava flour	1/0.62	6.43	12.11	13.7
Cassava starch	1/0.77	4.32	12.28	13.3
Corn starch	1/0.39	4.37	12.36	14.7
HIPIX 102	1/1.02	4.22	12.04	9.3
HIPIX 100	1/3.57	4.11	11.54	10.3
HIPIX 101	1/4.51	5.09	12.12	9.7
Potato flour	1/6.11	6,74	11.96	5.3

TABLE II
OPTIMUM STARCH/NAOH RATIO FOUND IN GELATINIZATION TESTS

Potato flour	HIPIX102	HIPIX101	HIPIX100	Cassava flour	Cassava starch	Corn starch
35.7/1	21.4/1	20.7/1	19.3/1	14.6/1	15.0/1	13.3/1

ACKNOWLEDGEMENT

The authors thank financial support from the Brazilian agencies CNPq, CAPES, FAPEG and FUNAPE. In addition, we like to thank Ingridion and Cargill for the samples donation, Federal University of Goiás and Goiano Federal Institute.

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