REMOVAL OF Ni AND V FROM AQUEOUS SOLUTIONS BY LIGNINS SUBJECTED TO OXIDATIVE TREATMENT WITH KMnO₄

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Abstract⸺ **Lignins were precipitated from Kraft black liquor to different acidic conditions; subsequently were subjected to oxidative treatment with KMnO₄. The oxidized material was characterized using IR spectroscopy for structural elucidation, and potentiometry in aqueous medium for determination of carboxylic groups. Among the trends, it found that the proportion of carboxylic groups in lignins increases with the oxidative treatment of the lignin. In addition with the IR were identified functional groups characteristic of lignin and showed also the changes caused by oxidative modification confirming the increase of oxidized groups when comparing the spectra of the different materials. Known the effects of oxidation on the lignins was evaluated adsorptive capacity of the oxidized lignin, showing that the oxidized lignin was able to adsorb up to 98% of Ni available initially, which corresponds to an increase in this ion sorption capacity of the double with respect to which only was precipitated. For its part, the lignin used to adsorb V decreased its adsorptive capacity, reaching only 19% of V fed. Based on this result was improved the experimental method of adsorption and the pH of process was controlled, thus it was obtained an increase of the adsorptive capacity of the material, reaching an adsorption of 91% of V fed. These results agree with the proposed mechanisms on how the metal ions studied in this work can be adsorbed.**

Keywords⸺ **Lignin, adsorption heavy metal, oxidative treatment.**
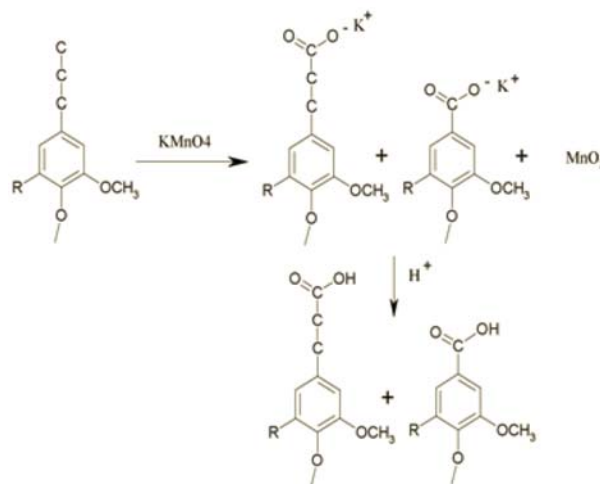
I. INTRODUCTION

At present the study of the potential applications of lignin has experienced a huge breakthrough. Your chances of utilization are based on their ability to perform functions such as chemical dispersant, binder, emulsifier and stabilizer of emulsions (Alonso, 2002). In addition, because many functional groups present in its structure have the ability to retain ionic species of a specific size and load, it has been raised its use as a potential bioadsorbent of heavy metal ions for wastewater treatment (Pérez *et al*., 2006).

Among the functional groups found in lignin can be mentioned: hydroxyl groups aliphatic and phenolic, also carboxylic groups which do not occur naturally in the lignin, but they are introduced as a result of the process of obtaining wood. All these groups in general serve as sites for adsorption of metal ions and other components (Lalvani *et al*., 1997; Palman and Khalafalla, 1988), hence is possible to considerer lignin as bioadsorbent.

On the premise of the use of lignin as a possible bioadsorbent of Ni and V ions (metals found as contaminants in waste streams from the process of demetallization of oil and Venezuelan oil coke) it was found that depending on the treatment in which lignins were subjected during their obtaining, they vary the proportion of functional groups present in its structure, which has an effect on the change of power ion adsorbent Ni and V. So, the ion adsorption process of Ni and V by the lignin is strongly influenced by the presence of such functional groups, it found that with increasing number of hydroxyl groups the greater the adsorption of Ni and with increase the amount of carboxylic acid groups the greater the adsorption of V, by completely different mechanisms depending on the pH of the solution (González, 2008).

Potassium permanganate (KMnO₄) is able to oxidize certain types of alcohols to aldehydes, ketones and carboxylic acids. Since lignin contains, among other groups, both aliphatic and phenolic hydroxyl, it is possible to take advantage of the oxidating action of the KMnO₄ over the lignin in order to increase the proportion of carboxylic groups, which could promote the adsorption of Ni by ion exchange, and of the V by the mechanism proposed by Tracey *et al*. (1990) where the carboxylic acid groups are capable of forming complexes with vanadate molecule.

Figure 1 shows the possible structures resulting from the oxidation of lignin by taking into account that the carboxylic acids are formed by the oxidation of primary alcohols, and also because the KMnO₄ is a strong oxidizing agent that can degrade aliphatic chains of the lignin, obtaining from them aromatic carboxylic acids.

Fig. 1: Structures resulting from the oxidation reaction of lignin

Table 1: Conditions of precipitation of the lignins.

Lignin	Ácid	Concentration (acid) mol/L	pH (final)	T (ºC)
L-Ni	H_2SO_4	1	4	**25**
L-V		0.1	2	

This paper aims to evaluate the effect of precipitated lignin oxidation using $KMnO_4$ as an oxidizing agent, by means of a description of its structure by way of infrared spectroscopy (IR) and the ability to adsorb both the Ni and the V of each of the oxidized lignins.

II. METHODS

A. Raw materials, materials and equipment.
• Black liquor derived from the processing of Caribbean pine wood [Kraft black liquor (KBL)].
• Atomic spectroscopy standard solution of Nickel chloride ($NiCl_2.6H_2O$) of 1000 ppm Fluka.
• Atomic spectroscopy standard solution of (meta) Ammonium vanadate (NH_4VO_3) of 1000 ppm, Riedel-de Haën (1.00 g vanadium-Standard alsmeta-vanadate wasserlöslich, für AAS).
• 98% concentrated H_2SO_4 Fluka.
• Potassium permanganate ($KMnO_4$).

B. Precipitation of Lignins
Of previous studies (Hernández, 2007) were selected precipitation conditions that originate lignins with better adsorption to Ni and V respectively. Then, it preceded to the characterization tests on these lignins.

Table 1 gives the conditions of precipitation for the lignin used in this study:

Precipitation of lignin from Kraft black liquor
The lignins were obtained by precipitation from KBL using H_2SO_4 as a precipitating agent to the concentration specified in Table 1, and for this we took an aliquot of 50 mL of KBL, with magnetic stirring was acidified with the acid solution corresponding until to the final pH. After reaching the final pH was left to stir during 10 minutes, then the precipitate was filtered by gravity on a Whatman filter paper Nº 4, and let drain at room temperature. The precipitate recovered, was placed in a petri dish and dried using a lamp at a temperature of 60-75 ºC for 90 minutes.
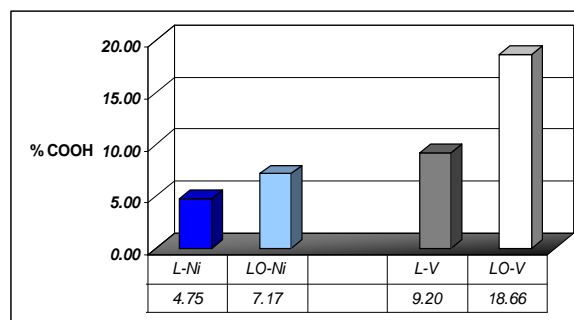
C. Oxidative modification of lignin by $KMnO_4$
It takes a sample of 1.5 g of lignin in a beaker and was added through a burette 50 mL of 0.15 M $KMnO_4$ slowly for 60 min under magnetic stirring. Then was filtered by gravity using Whatman filter paper No. 4 and the residue was dried in an oven at 65 °C (Rivas, 2007).

D. Characterization of lignins
Determination of carboxylic groups
The determination of carboxylic groups was performed using the technique of potentiometry in aqueous medium, method which determines the amount of such groups by direct titration with NaOH and the potentiometry is used to detect the equivalence point (El Mansouri, 2006).

Characterization by infrared spectroscopy (IR)

Fig. 2: Number of carboxyl groups present in the unmodified lignins treated with $KMnO_4$

The IR method used, was the KBr tablet with a sampling rate of 5% per gram of KBr in a team scores TENSOR 27 of 8 cycles, a resolution of 4 cm^{-1} and a range of work: 4000-400 cm^{-1}.

E. Adsorption process
Were prepared separately two synthetic solutions containing 20 ppm Ni^{+2} and V^{+5} from their respective standard solutions of concentration 1000 ppm. Each synthetic solution was 20 ppm at pH 4. Then they put in contact with 0.400 g of each of the lignins, precipitated with 100 mL of each of the synthetic solutions separately. The resulting mixtures were subjected to a process of agitation for about two hours, as described in Pérez *et al.* (2006). Next, it proceeded to filter each mixture at a vacuum filter using as a filter medium a porous glass filter. The concentration of metal ions in the filtrate was measured by atomic absorption process by the method of Inductively Coupled Plasma (ICP).

III. RESULTS AND DISCUSSION
A. Characterization of the lignins studied
Characterization tests were conducted on each of the oxidized lignins, the characterization consisted mainly in chemical methods for the determination of carboxylic groups, structural analysis and functional groups by IR spectroscopy.

Determination of carboxyl groups
According to the proposed mechanisms for adsorption of Ni and V, the quantification of these functional groups is of paramount importance. Since the carboxylic groups are involved in ion exchange reactions with metal ions which could promote the adsorption of Ni, and also, as Tracey *et al.* (1990), the carboxylic acid groups are capable of forming complexes with the vanadate molecule which could promote the adsorption of V. In addition, quantification of these groups provides information on the degree of degradation or depolymerization and modification of lignin (El Mansouri, and Salvado, 2007; Alonso, 2002). It also provides information about its solubility.

Figure 2 shows the results for the lignins under study.

In the precipitation of the lignin, as a result of further degradation by acidification, with decreasing the final pH of precipitation increases the amount of carboxyl groups in the structure of lignin (González, 2008). So as

it can see in Fig. 2, L-Ni material was acidified until pH=4 resulting with 4.75% of carboxylic group, and L-V that comes from black liquor acidification until pH=2 has a higher content of these functional groups (9.20%).

When oxidized with KMnO$_4$ can be seen that there is an increase in the proportion of carboxylic groups; it is noted that the oxidized lignins LO-Ni and LO-V, obtained respectively 7.17 and 18.66% of these groups, almost about twice with respect to lignins unoxidized.

In the oxidation lignin to adsorb V, it obtains an increase in the proportion of carboxylic groups, this increase should promote the adsorption of V according to the mechanism already proposed by Tracey *et al.* (1990) for the formation of complexes with vanadate. But one consequence of oxidative treatment with KMnO$_4$ in lignins precipitated, appears to be that gives buffering capacity that makes the solutions of Ni and V increase their pH once they are in contact with the lignin, from 4 to a pH of about 7, which assumes that the V because of its high oxidation state changes its speciation (Guzmán *et al.*, 2002). So, as the adsorbate changes, there is no control of the adsorption for the change in pH.

Moreover, the increase in carboxylic groups in the oxidized lignin favours the ability to adsorb Ni, since at the adsorption pH, the acid groups are partly deprotonated, which provides a surface charge density and with them lignin sites active for adsorption.

Infrared spectroscopy analysis

This study was performed by a collection of assignments to the peaks or bands of spectra of different lignins studied by Jahan *et al.* (2007). Table 2 is a compilation of the signals identified in the lignin spectrum selected for this study.

Overall, the study was conducted at two lignins before and after being oxidized which generated a total of four spectra that contain all the characteristic bands of lignin. Around 3400 cm^{-1} shows the band corresponding to the hydroxyl group (OH). The following is the characteristic band at 2930 cm^{-1} for the elongation of the link carbon hydrogen for methyl and methylene groups, as well as the presence of a peak at 620 cm^{-1} is synonymous of the presence of sulfur in the sample.

The Fig. 3 compared the unmodified adsorbents with greater adsorptive capacity of nickel (L-Ni) and with the highest adsorptive capacity of vanadium (L-V). The most noticeable difference between the two lignin precipitated, can see in the range around 1710 cm^{-1} a marked band that only appears in the spectrum of lignin used to adsorb vanadium (L-V), this value corresponds to carbonyl groups (C=O) non-conjugated in ketones and esters, and on the other hand, also corresponds to the conjugation with aldehydes and carboxylic acids substituted in position "p" (Singh *et al.*, 2005; Sarwar *et al.*, 2007), which agrees with the results of the quantification of carboxylic groups, where L-V lignin has a greater proportion than L-Ni lignin. Also can be seen in Fig. 3, differences in the relative proportion of two peaks at 1215 and 1245 cm^{-1} for the OH elongation of

the secondary alcohol, to the vibrations of the guayacil ring and the C=O stretching, respectively.
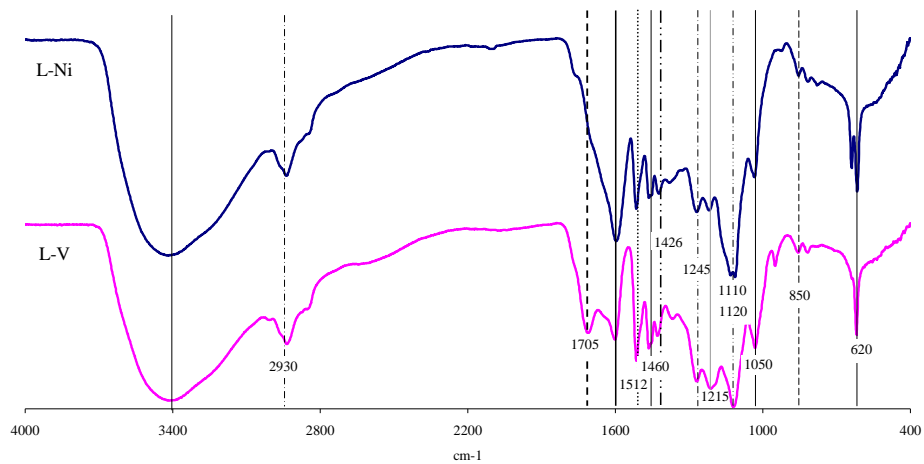
Around 1110 cm^{-1} shows a peak typical siringyl units of secondary alcohols and of carbonyl groups, which presents a greater proportion relative in the lignin L-V, which may be result from an increase in the acid treatment during precipitation (pH=2) which causes an increase in the proportion of phenolic group by the rupture of the β-O-4 bond (Nada *et al.,* 1998; 2000).

After oxidative treatment, and with the goal to identify the most important structures present in these modified materials, were compared with the spectrum of the compound from which they came, i.e., in Fig. 4 was compared the material with the highest adsorptive capacity of nickel (L-Ni), with that obtained by treating the latter with KMnO$_4$ (LO-Ni).
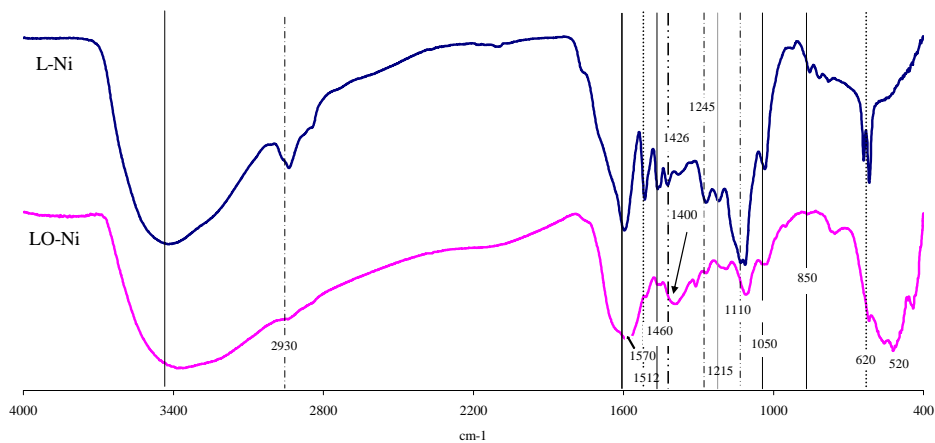
Table 2: Ranks of the absorption bands.

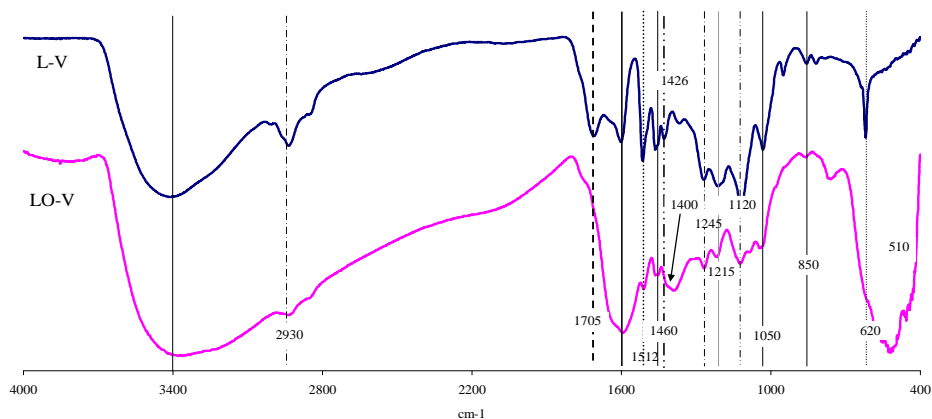| Band (cm^{-1})	Assignment
3400	OH stretching (H-bonded)
2930	CH stretching of methyl or methylene group
1710	C = O stretching
1600	Aromatic skeleton vibrations plus C=O stretching
1512	Aromatic skeleton vibrations (G > S)
1460	C-H deformations (asym in -CH3 and -CH2-)
1426	Aromatic skeleton vibrations
1390	Aliphatic C-H elongations
1335	Sirengil ring
1245	G ring plus C=O stretching
1215	C-O links in Guayacil estructures
1120	C-O links ether type
1050	Aromatic C-H in-plane deformation (G > S) plus C-O deform. in primary alcohols plus C-H stretching (unconjugated)
850	C-H out of plane (aromatic ring)
620	A broad band of C-S bond

Between the main differences that can be highlighted are observed in Fig. 4, the attenuation of the signal at 2935 cm^{-1} for the elongation of the link carbon hydrogen for methyl and methylene groups and methoxyl groups. In addition to the widening of the band corresponding to stretching of OH, with a shoulder that extends from 2200 cm^{-1} to the band of OH groups, which may be indicative of the OH from these carboxylic acids with these characteristics (Thielemans and Wool, 2005). Note also the widening of the peak around 1600 cm^{-1} in the spectrum of lignin LO-Ni, corresponding to the vibrations of the aromatic ring which presents this bandwidth by the presence of carboxylate groups, due to that these have an asymmetric stretching near 1650-1550 cm^{-1} and a weaker one near 1400 cm^{-1} in the IR (Silverstein *et al.*, 1974), which were increased in significant proportions by treatment with KMnO$_4$. It can also be seen in the spectrum of lignin LO-Ni the relative decline of signals 1110, 1215 and 1245 cm^{-1} which express the presence of secondary alcohols and stretching C=O groups, which is a result of the transformation of the alcohols toward its corresponding oxidized form by treatment with KMnO$_4$.

Fig. 3: IR spectra of unmodified adsorbents.

Fig. 4: IR spectra of unmodified and oxidized adsorbents with higher adsorptive capacity of Ni.

Fig. 5: IR spectra of unmodified and oxidized adsorbents with higher adsorptive capacity of vanadium.

In Fig. 5 show the spectra of the material with the highest adsorptive capacity of vanadium (L-V) and the corresponding treated with $KMnO_4$ (LO-V), the result is homologous to that of Fig. 4. Note that the peak of C=O stretching around 1710 cm^{-1} is overlapped by the bandwidth centered at 1600 cm^{-1} in the spectrum of lignin LO-V, which is a result of the increase of carboxylate groups as a consequence of the oxidation with $KMnO_4$. Note also the appearance of a signal at 510 cm^{-1} of great intensity in the spectra of lignins LO-Ni and LO-V, characteristic of metal-oxygen bonds, that overlapping the signal at 620 cm^{-1} which is assigned to C-S compounds.
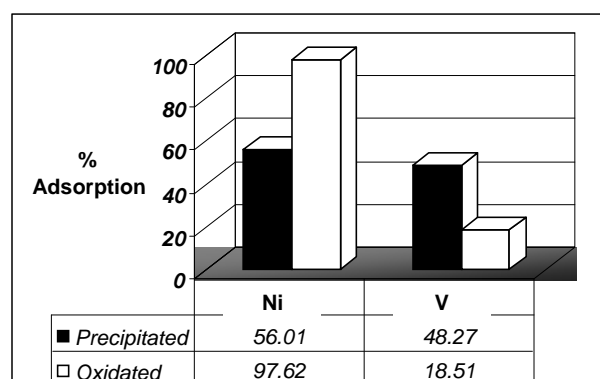
Figure 6. adsorptive capacity of Ni and V precipitated and oxidized lignins

B. Evaluation of the adsorptive capacity of the adsorbents studied.

Once obtained the adsorbents were evaluated their capacity to adsorb the ions of Ni and V in order to verify the changes in the adsorptive capacity that resulted as a consequence of the different treatments. The Fig. 6 gives the percentages of lignin adsorption obtained for each study.

As it is shown in Fig. 6, the lignins precipitated in general show changes in the adsorptive capacity of Ni and V, when are subjected to oxidative treatment. Lignin used to adsorb Ni showed a significant increase in adsorptive capacity of a 56-97% Ni adsorbed; in turn the lignin used to adsorb V, decreased its adsorbent power by more than 50%.

From previous studies (González, 2008), it was proposed that the adsorption of Ni was ruled by a ion-exchange mechanism via the formation of chelates between the Ni ion and hydroxyl groups phenolic and carboxylic groups present in lignin, and that this mechanism depends strongly on the pH of the solution because, when the pH is greater than 6, both carboxylic groups and phenolic hydroxyl-groups, are deprotonated or partially desprotonated (Patnaik, 2004), which facilitates the exchange and increases the quantity of Ni adsorbed for these lignins.

As for V, in previous studies (González, 2008) was found that as increasing the amount of carboxylic groups in lignins precipitated there is an increase in the adsorptive capacity of the ion. In this work it was assumed that the vanadate (which is ionic species with which it was worked to prepare the solution according to the distribution of vanadium that Guzmán *et al.* (2002) presented in their work) tends to form complexes with mono and dicarboxylic groups in lignin such as the mechanism described by Tracey *et al.* (1990). Similarly in a previous paper (Núñez, 2006) was noted that the precipitated lignins which had the best adsorption of V decreased the pH of metal solutions from 4 until approximately 3, indicating the higher proportion of acid groups in these lignins to which V is affine.

The lignin precipitated after treatment with KMnO$_4$ increased the pH of the metallic solutions until around 7, indicating the basic features of these lignin and that

carboxylic groups who are in greater proportion would be kind of carboxylate (COO$^-$); reason why the mechanism described by Tracey *et al.* (1990) does not apply in this case due to the pH at which adsorption takes place.

In addition to, this mechanism is only true if the species V with which it is working is vanadate, which depends on the pH (Guzmán *et al.*, 2002). Therefore the decrease in the adsorptive capacity of the lignin used to adsorb the V to be oxidized with KMnO$_4$, is due to that the adsorbate is not in the ionic form that allows it to be trapped by the adsorbent, and not by the presence of more active sites due to oxidation.

To check the pH dependence of adsorption on the ability to adsorb to the lignin were conducted with Lignin oxidized toward V two additional tests, the first without control of pH of adsorption and the second with control of this variable. To rule out the possible interference of KMnO$_4$ residual, the lignin underwent a process of cleansing that consists in a washing with distilled water at pH of precipitation to prevent solubilization of the lignin. The results are summarized in Table 3.

Table 3: Adsorptive capacity of lignin oxidized with purification treatment and control of pH.

Adsorption Process: Lignin(LO-V)	% Adsorption	initial pH	Final pH l
Adsorption of V	51.69	7.84	7.80
Adsorption of V (pH control = 5)	79.90	7.84	5.05

After purification, the adsorption of V was increased, indicating that residual KMnO$_4$ possibly interferes with the adsorption process but anyway the increase is not significant compared with the precipitated lignin unoxidized. However once controlled the adsorption pH to acid pH, by adding a drop of concentrated HCl, there was an increase of the adsorption of 79.90% of V adsorbed for a value of pH = 5, thus demonstrating the dependence of pH of the two mechanisms of adsorption.

IV. CONCLUSIONS

The oxidative treatment increased the proportion of carboxylic groups, mostly in the form of carboxylate, which favors the adsorption of Ni, this increase in carboxylate groups does not favor the adsorption of V by the increase in pH of the solution.

The mechanisms of adsorption of Ni and V are strongly dependent on the pH of the solution. The adsorption of Ni is favored at pH values above and equal to 6, and the adsorption of V is favored at pH below 5.

ACKNOWLEDGEMENTS

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