"Effects of Liming on Some Physico-Chemical Properties of Copper mine Tailings amended Soil of Khetri Area".

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DEDICATED TO

THOSE, WHO ARE WORKING FOR
THE CAUSE OF ENVIRONMENT

CERTIFICATE

The research work embodied in this dissertation entitled **"EFFECTS OF LIMING ON SOME PHYSICO-CHEMICAL PROPERTIES OF COPPER MINE TAILINGS AMENDED SOIL FROM KHETRI AREA"**, has been carried out in the School of Environemntal Sciences, Jawaharlal Nehru University, New Delhi. This work is original and has not been submitted in part or full for any other degree or diploma for any University.

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CHAPTER - 1

INTRODUCTION

INTRODUCTION

Surface mining and ore processing cause profound changes in landform and bear little or no resemblance with the undisturbed soil (Wali and Kollman, 1977) and creats both waste disposal and land degradation problem. Tailings generated from mining process may be devoid of or may contain very little amount of organic carbon, may have very little source of nitrogen and may be deficient in available phosphorous, potassium and other micro nutrients essential for plant growth (Boyum et.al. 1978). For instance in the case of tailings obtained from copper mining at Khetri, Rajastahan, India, contain small amount of organic carbon, nitrogen and are dificient as well in terms of availbility indexes of pottassium, phosphorous. However, they possess an appreciable amount of heavy metals essential for plant growth and better soil environment.

Tailings, when due to various operations, are brought to the field cause heavy damage to the soil. Tailings spread on the field cause severe changes in soil environemnt which are unfavourable for proper plant growth. Alternatively we can say that the surface mining and ore processing cause severe environmental degradation in the landform (Adrson, 1970). Thus reclaimation of the degraded land due to surface mining and ore processing constitutes an important aspect of environemntal problem.

As far as land reclaimation is concerned, approaches to be employed depend upon the nature of degrading agents and some local factors, such as soil properties, climate etc. There are generally three accepted approaches, depending upon the various factors, which are frequently employed for land reclaimation. These approaches include, biological i.e. vegetative methods, chemical approaches and mechanical or engineering practices. All above said approaches may be applied separately or simultaneously depending on the severity of the problem. Out of the aforesaid reclaimation approaches, vegetative or biological methods are most preferred one from the ecological point of view (Ernst, 1974, 1982, Bradshaw, 1975). Chemical approaches for land reclaimation are generally application of a foreign agent, which is a chemical or any substance containing required chemical either in combined or uncombined form, which can ameliorate the soil envioronment. Chemical process are although less common, could be considered as a supplement to the biological and egineering practices to reclaim the degraded land. Yet, it's importance in the cases where waste disposal problem exists simultanously with land degradation due to the surface mining, cannot be overlooked.

Hindustan copper limited is engaged in producing finished copper metal with an annual capacity of approximately 31,000 million tons at khetri copper complex. About 85% ore after its processing is rejected as a waste material called tailings. Pollutants Comming out of this plant can be classified into two categories : (1) Dust generated in the crushing action as well as harmful gases from sulfuric acid and other plants causing air pollution and (ii) solid waste disposal as tailings and slurry spillages as well as mine effluents causing water land pollution. Initially the problem of disposal of tailings posed a big threat for water and land pollution, but the problem was temporarily solved by developing a tailing pond at a distance of 1.6 kms away from the plant side. The dam with a capacity of 9 million cubic meters is spread over an area of about 0.975 million square meter.

Tailing obtained from copper mining area, khetri have an appreciable amount of total phosphorous, and potassium, esential nutrients for plant growth and some heavy metals. So any mechanism or process which can release the macro and micronutrients contained in tailings, shall supplement the plant growth and provide a better soil environemnt. Henceforth, the aforesaid possible mechanism not only results into land reclaimation of the degraded land due to surface mining and ore processing but also may provide a possible method of tailings disposal management.

Tailings obtained from Khetri copper mining area are highly acidic (pH 3.95), whereas soil adjoing mining area are near neutral (pH = 7.12). So mixing up of tailings with soil in different proportions will give a fairly acidic mixtures of soil and tailings. As we know that the plant growth is best in the neutral pH range of the soil. Therefore any third agent, which is able to neutralise the soil - tailings mixtures can indicate (1) the possible reblease of nutrients (2) any other benifical effects due to the presence of tailings and (3) its negative effects, with or without the presence of third agent. Physio - Chemical parameters are indexes for the quality of the soil environment and fertility of the soil. From the physio - Chemical parameters alone, future utilization of soil with or without further amendments can be predicted. Thus physio-chemical parameter can direct us about the exploitation of nutrient content of tailings concerned which are otherwise waste materials. Physio-chemical parameters chosen for the present study include pH, EC, organic carbon, total and availble nitrogen, phosphorous, pottassium and few selected heavy metals (Cu, Fe and Zn).

To remove the acidity of soil or soil mixtures, commonly used materials are oxides, hydroxides or carbonates of calcium and magnesium. These compounds are preferred to as "agricultural limes" (Adam and Pearson, 1967). They are realtively inexpensive and leave no objectionable residue in the soil (Barber, 1967). Among the compounds of alkaline earth metals, oxides, hydroxides or carbonates of calcium are commonly preferred (barber, 1967). In the present laboratory study, calcicum oxide (CaO) (Reagent grade) is chosen for neutralising the acidity of soil-tailings mixtures, since CaO has potential as Liming material (Kargbo, 1986).

It has been found that liming has always some beneficial effects on acid soils in correcting soil environment. Moreover, the soil taken for present study is neutral (pH = 7.2), but when mixed up with tailings in different proportions gives acidic mixtures.

It will be worth considering to study the effects of liming in terms of physio - chemical parameters on the soil which is neutral, but mixed with acidic copper tailings. Thus, the present study attempts to fulfil broadly two objectives, firstly, to develop an approach towards tailings disposal management and secondly, a way to exploit the micro and macro nutrient contained in copper tailings along with land reclaimation.

CHAPTER - 2

REVIEW OF LITERATURE

REVIEW OF LITERATURE

All mining activities create an imbalance in the environment by altering landform and physiography, disrupting the hydrologic cycle and discharging wastes into the rivers and polluting them with toxic substances. Thus mineral development activities inevitably disturb the environment. Milling operations i.e. ore milling and concentration produce tailings, which if not properly disposed, could easily find their way into the surrounding natural environment and creates a variety of environmental problems, including air, land and water pollution. So the most common problem of the mines is how to dispose of the mine tailings properly. If disposal could be associated with a benefit to plant growth, a dual advantage would be realized.

Tailings from mineral operations can be stored as upland or underwater disposal including backfilling of mined out areas (Andrews, 1975). The bare surface of above ground disposals are open to erosion by water and wind without a protective vegetation. Therefore, the final aim of managing these sites is primarily to diminish the environmental impact on the surrounding landscape by stabilizing these dumps by vegetation because technical solution have proved to be insufficient (Greszta, 1973, and Barner, 1978).

Mine tailings often lack organic matter and essential plant nutrients and contain excessive concentration of metals that are toxic to plants, hence these wastes are devoid of vegetation (Bradshaw, 1952).

TAILINGS MANAGEMENT AND LAND RECLAIMATION

Upland disposal of mine wastes are generally characterized by some properties which are hostile at least in combination to plant growth (Briones, 1987 and Ernst, 1988).

1. High levels of various heavy metals and other elements. (Bradshaw, 1952)
2. Low amount of major plant nutrients, (Deans and Heavens, 1973).
3. Lack of microbiological population (Briones, 1987).
4. Poor physical structure.

These factors make the establishment of vegetation difficult. So, for good vegetation development some way must be found to overcome or at least to modify the hostility of some of these environmental factors to higher plants. Attempts have been made to restore mined lands, including surface amelioration using inert materials and direct revegetation involving tolerant or non-tolerant plants.

Metal - tolerant plants have highest potential for a successful natural revegetation of these mine tailings (Ernst, 1974 and 1982; Bradshaw, 1975). Dean et. al. (1974) and Williamson and Johnson (1984) found that stabilization of toxic materials by vegetation establishment is generally superior to alternative techniques. Smith and Bradshaw (1972) had shown the practical value of using tolerant varieties on mine tailings.

In the past technical complexing agents such as EDTA has been applied to reduce the concentration and toxicity of heavy metals in mine tailings but was found an expensive management (Ernst, 1981).

Pyrite bearing tailings present a particular problem in establishing vegetation, since upon oxidation the pyrite yeilds sulfuric acid and in consequence increasing acidification of surrounding medium (Dave et.al. 1985; Ivarson, 1973 and Pulford, et. al., 1983). As long as neutralisation of acids by carbonates can occur plant root will not be affected. If the neutraliation capacity has been lost, a change in soil pH will increase the availability of heavy metals and that of A1 to higher plants. Upto now, only a few plant species are known to evolve A1 tolerance in addition to metal tolerance (Ernst, 1988).

Mine tailings and disposal sites have often a high imbalance of the major and minor nutrients (Ernst, 1974 and 1982; Smilde and Van Driel, 1977). In addition to high amounts of those heavy metals, which are minor nutrients, but which ocur in concentrations typical for major nutrients, there is an acute shortage of major nutrients.

A wide range of commercially available non-tolerant plant materials were used for reclaiming copper tailings at Pima mine (an open-pit copper mine) in Arizona. Ludeke (1973) concluded that ultimate objective of maintaining the natural environment in disposal area had been achieved by the success of the vegetative stabilization.

In an another experiment at Pima mine, four soil materials - desert soil, copper overburden, overburden plus tailings and tailings were tested for the growth five tree species. It was revealed that desert soil had the highest productivity., over burden plus tailings and tailings in decreasing order (Day and Ludeke, 1980). Subsequent experiments involved planting three legumes (Day and Ludeke, 1981) and six perennial grass species (Day and Ludeke, 1982), and yielded similar result, indicating that over burden might be a convenient source of reclaimation material.

Tailings obtained from the processing of lead, zinc and copper ores at Mount Isa, North Australia, was amended with reverberatory furnace slag, organic residue from sewage, straw mulch and fly ash. Identical species, seeding rates and fertilizer additions were used for all treatments. It was discovered that the best amended treatment was incorporation of fly ash (Ruschena and others, 1974).

Gadgil (1969) reported that in revegetating zinc and copper smelter at Lower Swansea valley (UK), domestic refuse, organic fertiliser, lime and sewage sludge were added before planting several tolerant population and grasses. Goodman and others (1973) suggested that annual dressing of inorganic fertiliser and the application of organic matter was required to maintain the vegetative cover on zinc, copper and iron wastes in Swansea Valley. But these results are non-conclusive. In general, the amendment of organic waste in conjuction with the addition of lime and fertilizer increases the growth of tolerant population and grasses. However, plants established on organically amended wastes showed retardation after 12 months because decline in nutrient level and gradual lowering of organic matter status (street and Goodman, 1966). Similarly Gemmel (1973) found that regular application of fertilizer are necessary to ensure a continuos supply of nutrients and to prevent any deterioration of the established vegetation.

Commercial grass seed mixtures were also used in reclaimation of copper tailings area near sudbury, Ontario, Canada. Feed grade lime (7.5 tonnes/ha) and fertilizer of 5-20-20 (N-P-K, 480 Kg/ha) were applied followed by seeding and another application of 5-20-20 (N-P-K, 336 Kg/ha). Once grass was establihed, the annual maintenance consisted of (a) 90 Kg of 5-20-20 (N-P-K) fertilizer applied immediately after cutting, and (b) Urea applied at the rate of 129 kg/ha in late fall (Peters, 1970).]

Tailings generated at Captains flat mining area in Southern New South wales contain principally Fe, Zn, Pb and Cu as sulfides and are acidic and toxic (Craze, 1977). Pinkerton and Simpson (1977) examined nutritional aspect of establishing suitable plants species following the lime application to reduce the uptake of heavy metals by raising pH. They found that liming effectively reduced the content of zinc to acceptable levels in all three species grown on soil mixtures and allow the plants to grow normally. However, in early attempts at reclaimation Keane (1977) applied lime and found depression in test species to occur on limed wastes from mine.

Lipsett et. al. (1979) studied the nutrition of oats, subterranean, clover and poplar grown in contaminated material and in mixture of it with an uncontaminated control soil. For all species high acidity and availability of zinc were principal factors that were counteracted by application of lime. However, a depression in growth of clover in both soils was observed with high rates of lime. This was subsequently shown to be associated with Boron deficiency.

Attempts have been made to reclaim copper tailings containing 0.069% copper by distributing innoculated seeds of Desmodium intortum into tailings to a depth of about 10 cm at Bougain Ville in papua, New Guinea. It was confirmed that Eucalputus can be used as pioneer growth on the tailings, provided there was sufficient nutrients. The absence of naturally occuring nitrogen and severe deficiencies of phosphorous made artificial fertilizers necessary for securing establishment (Hartely, 1976). Penafil (1981), on the basis of two year data on mine vegetation revealed that some plants are suitable for mine wastes planting in Baguio district.

Dean and Heavens (1973) found that topsoil and organic substrates, such as sewage sludge and peat, serve as surface amendments for tailings waste. Furthermore, organic matter complexes heavy metals, which are therefore unavailable to plants and it improves water holding capacity.

Hay or barley straw have been suggested as a mulch on copper mine tailings and has several advantages. First, it stabilizes the soil temperature and thereby generating a better environment for seed germination. Second, it permitts the soil to absorb moisture and thirdly, it enriches the growth of micro-organisms (Ludeke, 1973).

Craze (1977) found that an impermeable and continuous 15 cm clay and soil layer provided a medium for the vegetative cover. After the addition of top-soil layer the area was cultivated, sown with legumes and grasses, limed and fertilized with nitrogen, phosphorous and potassium in the ratio 2:3:12. It decreased the acidity and a marked reduction in concentrations of metallic salts in solution.

Goodman and others (1973) showed the importance of fertilizer treatments and the use of tolerant plant populations. It was indicated that, in the presence of fertilizer (N, P and K) copper tolerant Agrostis tenuis thrived in pure copper waste.

Tailings dams should be stablized and reinforced through vegetative covering. The use of some biological structures in stabilizing tailings dams had ben tried (coastales and coastels, 1983 and coastales and others, 1981 and 1982).

Numerous attempts have been made to find some agricultrual use for pyrite mine wastes (McGeorge, and Breazeale, 1955; Shkolnik and Markorova, 1951; Smith, 1930 and Stroenlein and Berger, 1963).

Smith (1930) studied Sulfur Oxidation with copper carrying pyrites (1.26 to 1.63% Cu) on varrying soil and showed that crops did not indicate copper toxicity with amounts of pyrite used and also showed that pyrites carrying small amount of copper, may be safely applied to calcareous soils in fairly large amounts. acid soils should be treated with care unless lime also is used.

McGeorge and Breazeale (1955) and Smith (1930) reported that certain oxidised pyrites have been demonstrated to be of agricultural importance, when applied to soil or to plants.

Maclean and Dekker (1976) studied the lime requirement and availability of nutrients and toxic metals to plants grown on six acid pyrite - bearing mine tailings, varying in pH from 1.9 to 2.9. They found that amount of $CaCO_3$ required to neutralise the initial acidity and that generated during cropping in four of the samples containing less than 5% Sulfur varied from 10,000 to 50,000 ppm. The acidity of the other two samples, which contained high amount of Sulfur, was corrected by liming initially, but the pH were less than 2.5 at the end of the cropping period, despite high addition of $CaCO_3$. Reed canary grass was grown successfully in the limed and fertilized tailings. With inadequate lime, the soil became very acid and released relatively high amounts of Mn, Fe and Al to the plants. Recovery of added K by extraction with 0.1 N acetic acid decreased with increasing acidity of tailings. The low recovery of fertilizer nutrients extracted from the extremely acidic uncropped tailings indicates the necessity to raise the pH to a level favourable for plant growth and nutrient utilization.

Unpublished data of the author showed that a lime-digested sewage sludge in addition to supplying organic matter, was an effective liming material and an excellent source of nutrients for Reed Canary grass.

We can say that revegetation is the best alternative as far as land reclaimation of the degraded land due to mining activities are concerned. But prior to every revegetation, a careful analysis has to be carried out to analyse the speciation of heavy metals, the amounts of major plants nutrients, the water holding capacity, physical structures etc. to evaluate the potential of the ecosystem to support the vegetation. Hence, to overcome the problem of highly acidic soils, Chemicals viz. lime must be judiciously used to restore the balance of that Ecosystem.

LIMING AND NUTRIENT AVIABILITY

The soil facotr in plant growth and mineral nutrition is a complex one, involving as it does interrelation between ion exchange characteristics, saturating ions, biological acitivities and a host of other variables. When an acid soil is limed, many facets of the soil enviornment are changed. Responses of crops to lime generally have been attributed to changes in the soil environment with regard to : (i) Solubilities of toxic substances, aluminium and managanese being those implicated most frequently; (ii) availability of calcium and magnesium ; (iii) availbaility of phosphate and potassium; (iv) solubilities and availabilities of trace elements; or (v) populations and activities of soil micro-organism.

Beneficial effects of liming are largely due to inactivation of toxic substance either aluminium or manganese or both. Mate et. al. (1972) found that alfalfa yield on an acidic soil greatly increased by liming and the increase in the yield was correlated with decrease in aluminium and manganese contents. The effect of liming in reducing aluminium and manganese toxicity is more due to increase in pH than the effect of calcium or magnesium ions (Gupta, 1970).

Bolton (1977) found that small limestone applications increased soil pH to values predicted by lime-requirement determination using a standard adsvisory method, but the larger limestone application increased proportionally less.

NITROGEN :

Liming of acidic soils generally increases the mineralization of soil organic matter. Gernally, liming of acid soils was found to have stimulatory effect on mineralization (Alexander, 1965; Edmeodes et. al., 1981 Harmson and Schreven, 1955). However, maginitude of this effect depends on the initial soil pH, rate of liming, moisture content and soil organic matter.

Allison and Sterling (1949), while experimenting lime on a number of mineral soils, found that liming had in all cases a very stimulatory effect on mineralization and the effect was maintained for a long time. In original soils, the amount of mineralized N per unit of total nitrogen was higher with soil of higher total nitrogen content. This difference was nearly levelled off after liming. Schachtschabel (1953) reported careful laboratory experiment on the effect of liming. The addition of lime resulted in an increase in nitrogen mineralization.

Hwang and Frank (1938) extended their investigation of the ammonification and nitrification in soils over a wide range of conditions (reaction, moisture content, aeration, temperature etc.) and formulated the important general rule that nitrification is much more restricted to optimal conditions than ammonification. Since ammonification is still significant in all extreme cases. The result is formation of NH_4 both at too high and too low pH, too high and too low temperature and so on.

Cornfield (1953), using a nearly neutral soil clay (pH 6.65) studied the effect of artificial acidification to pH about 4.0 by addition of sulpher. The overall mineralization of nitrogen was significantly reduced thereby a nearly complete supression of nitrification, the ammonification decreased only slightly consequently NH_4 accumulated in the acidified samples. Liming these acidified soils practically restored to original conditions. On the other hand when Thompson et. al. (1954) incubated 50 soils of pH 5.2 - 8.1 mineralization of organic N was not significantly correlated with soil pH.

It is well known that soil acidity restricts nitrification i.e. last phase of mineralization than ammonification in soils. The latter still being slightly active even a pH level around pH 4 (Harrisen and van Sehreven, 1955). Alexander (1961) and Scarsbrook (1965) found that liming produces a long term increase in the rate of conversion. This view is based on a number of laboratory and lysimeter experiments in which liming decreased soil content of organic matter (Jolivet and Helias, 1953; Kappen and Scharpensell, 1951), or in which liming increased the production of mineral N carbon dioxide (Allission and Sterling, 1949; Cornfeild, 1952; Voorhees et. al., 1907). On the other hand there is limited evidence indicating that soil acidity does not restrict mineralization of organic matter (Thompson et. al., 1954) and that the increase in mineralisation after liming is short-lived (Frercks & Kosegarten,. 1956; Mulder, 1950, Sehaehtschabel, 1953).

Awad and Edwards (1977) and Cullen and Grigg (1971) have suggested that the benificial effect of liming on the mineralization of soil organic matter is a reason for lime responses in the field. Edmedes et. al., (1981) found that effect of lime on two soils markedly increase growth above soil pH 5.8 - 6.0. Barrow (1965) in glass house experiment has shown that N-uptake by rye grass increased with increasing soil pH, due to liming and these results corresponded to feild trial results.

Borthakur & Muzumdar (1968) found that liming increased average mineral N-content of the soil significantly under low moisture, but under water logged conditon the difference was not significant.. .

In an experiment it was found the $CaCO_3$ at 0.4% and 0.8% level increased the pH of soil soil solution and $CaCO_3$ at 0.4% saved the plants from death and enabled them to produce a moderate amount of straw and grain, and at 0.8% $CaCO_3$ doubled this straw and grain yield (Nhung and Ponnamperuma, 1966).

Nyborg and Hoyt (1978) found that the increases in mineralization of N due to liming correlated with total N, C/N ratio and pH. The increase in net mineralization of N with increasing rate of lime application has been reported by Edmedes et. al., (1981) jwho observed that the numbers of ammonium and nitrate oxidising bacteria tend to increase with increasing lime application.

Liming at pH 5.0 - 5.5 is the critical range where all the bio-chemical factors are favourable in releasing more nitrogen from soils (Adhikari and Ganguli, 1971). They further noted that on additon of lime to soil at pH 7.0 to 8.0 release of N is alwasy less in presence or absence of organic matter than on liming at pH 5.0 to 5.5.

Nitrifying bacteria are quite sensitive to changes in the environment and their population is generally limited by ammonium concentration. Since numbers are greater in alkaline and neutral soils, liming may increase activity in acid soils (Dancer et. al. 1973 and Morril and Dawson, 1967). However, Pang et. al., (1975) found a decrease in nitrification rate with lime addition to an acid soil (pH 5.4) during a 6 week incubation period.

Singh and beauchamp (1986) studied the effect of liming on mineralization and soil nitrifier acitivity with mineralization in both soils. A significant increase in N-mineralization due to liming occured in both soils only when pH was raised above 6.0.

PHOSPHOROUS :

One of the primary reasons commonly proposed for liming acid soils is to increase phosphate availability to plants (Sanchez and Uehara , 1980). Increase in the availability of soil phosphorous is often cited as one of the principal benefits of liming on mjineral soils. However, conflicting views are held as to the effects of liming on the phosphate supplying power of acid soils. Liming has been reported to increase (Awan, 1964; Griffin, 1971; Rayden and Syers, 1975 etc.), decrease (Anderson, 1980; Mokwuryl, 1975; and Murrman and Peech, 1969) or not to affect (Janghorbani et.al., 1975 and Martini et.al., 1975) the phosphate that can be extracted from such soils. Similarly, the phosphate content of plants has been observed to increase, decrease or remain unchanged following liming (Amarasiri and Olsen, 1973; Janghorbani et.al., 1975) and Jones and Fox, 1978).

Liming acid soils is a common practice in the humid regions of the temperate zone and the studies of various workers (Cook, 1934; Ford, 1952; Midgley, 1941 and Salter and Barnes, 1935) indicate that lime helps to increase the availability of phosphorous to plants. Ignatieff and lemos (1958) have stated that, in the tropics, crops do not alwasy respons to liming at a certain pH to which they would response in the temperate regions. Russel (1961) reported that in the tropics and sub-tropics liming only improves crop yield on very acid soils and usually reduces the yields on moderately acid soils.

Naftel (1937) showed that readily available phosphorous was greatly increased more that doubel by the additon of lime. Askinazi & Yorsusov (1928) showed that introduction of lime in a podsolized soil resulted in an accumulation the mineral phosphoric acids in the soil solution and an increased phosphate solubility in weak acids. Cook (1935) showed that the addition of lime to soils caused significant increases in the amounts of readily available soil phosphates. Ghani and Aleem (1942) studied the effect of liming on the transformation of phosphorous in acid soils and found that available phosphorous regularly increased with time in all treatments with different materials, at all doses. They found that the order of effectiveness in increasing phosphate availability was.

$$MgO > Ca(OH)_2 > CaCO_3 > CaSO_4.$$

Kargbo et.al., (1980) studied the effect of lime on soil pH and phosphorous availability with different liming materials and found that pH and phosphate availability was increased with all lime types with all times. Black (1957) also showed that availability of soil phosphate to plants appears to increase as soils are limed to the vicinity of neutrality. Many studies have shown that increasing the pH of soil increases the amount of P extracted by resins and various extracting solutions (Kaila, 1965; Lankanen and Vuorinen, 1963; Murrmah and Peech, 1969; Parks, 1965; Rathje, 1961; and Taylor and Guerney, 1965).

Awan (1964) investigated the effect of lime on the availability of phosphorous in Zamorano soils as measured by crop response and soil analysis and found that major part of potentially available phosphorous in zarmorano soil is in organic form and liming of these soils liberated soil phosphorous from organic fraction. Greater availability of

P to plants resulting from liming has been reported by other workers also (Fox et.al., 1962, Rai et.al., 1963 and Thomas, 1961; Rai et.al., (1963) showed that the liming increases the availability of phosphate in an acidic red loam soil. Tripathi and Pande (1971) working on the acid lateritic sandy loam observed that liming to raise soil pH from 5.2 to 7.2 resulted in increase P-content of wheat grain and straw. Two seperate approches have been applied to phosphate solubility and fixation in soils (sample, 1980). One is based upon the "solubility product principle" postulating the formation of various phosphate compound by precipitation, and second is based upon theories of absorption on the surface of hydrated oxides of Al & Fe and clay minerals. (Larsen, 1967; Lindsay and Stephenson, 1959; Olsen et.al., 1977 and Toth and Bear, 1947). There seem little doubt that in acid soils, hydrated Al and Fe oxides are the dominant phosphate absorbing surfaces (Juo and Fox, 1978; Loganthan and Fernando, 1980 and Parfitt, 1978). Maximum absorption on such surfaces occurs at slighly below pH 4 (Parfitt, 1978) or slightly high than pH 4 (Herrandez and Burrham, 1974). Bowden et.al., (1980) and Obihara and Russel (1972) showed that phsophate absorption is maximum in the pH range 2 to 4. Danilo and Burrham (1974) indicated that phosphate sorption is known to decrease with increasing pH. The phosphate absorption chracteristics of Fe and Al oxides have been studied extensively (Bowden et.al., 1980; Hingston et.al. 1967 and Parfitt, 1978). Borah and Nath (1980) studied the effect of pH on transformation of phosphate in alluvial soil a found decrease in Al-P and Fe-P fraction and increase in Ca-P and occuluded Fe Fraction of Phosphate in soils. Similar results have been shown by Nath and Ghose (1981).

pH may be expected to be one important factor in determing phosphate sorptivity. When increasing application of lime are applied to acid soils, there is also possibility that increasing concentration of Ca may be affecting phosphate sorption (Helyar et.al., 1976). In general liming has been found to increase the availability of phosphorous in acid soils. Many experimental result show that liming above certain pH not only decreases the availbaility phosphorous in soil but also P-uptake by plants. Pierre and Browning (1935) found that plant growth decreased and phosphorous deficiency symptoms appeared when soils were limed above pH 7. Similar results were reported by many workes (Awan, 1960; Barnes, 1960; Fox et.al. 1964; Bhaumik and Asthana, 1969).

Hernandez and Burrham (1974) found no significant correlation between pH and phosphate retention for a group of mixed soils, but a group of pedologically similar soils differing mainly in pH gave a highly significant decrease in retention with increasing pH. They concluded that pH may be expected to be one of the important factors in determining phosphate sorpitivily, its role in mixed population of soil is evidently masked by variations in other soil properties. Reeve and Summer (1970) and Lucas and Blue (1972) using field treatments came to the surprising conclusion that Liming did not reduce the phosphate sorptivity of certain tropical soil.

Both concentration of electrolytes and species of cations are known to affect phosphate sorption and desorption by soil and oxide surfaces (Barrow and Shaw, 1979; Brrow et.al., 1980; Ryden and Syers, 1975 and Singh and Tabatabai, 1970).

In addition to purely chemical aspect discussed previously, liming may have an effect on phosphate availability through micro biological process. Seveal workers (Awan, 1964; Halstead et.al, 1963) have observed stimulatory effect of lime on mineralization of soil organic phosphorous. Awan (1964) found that liming two soils from pH 5.5 to 6.5 resulted in organic phosphorous as a % of total phosphorous, being reduced from 83% to 74% after a 2 year period. Halstead et.al. (1963) showed that liming dresulted in an average decline of 3.6% of the total organic phosphorous and provided evidence of mineralization of organic phosphorous following liming. Organic form of soil phosphorous may undergo mineralisation (Bower, 1949; McCall et.al., 1954; Thompson and Black, 1948 and Thompson et.al., 1954), although the extent of this transformation may be expected to vary with soil conditons. Russel (1950) suggested that the beneficial effect of lime on phosphorous availability is due, at least in part, to the transformation of organic phosphorous to a mineral form, particularly since liming increases the rate of decompositio of soil organic matter. Few other investigations on release of phosphorous from organic form, following the applicaton of lime, have been reported (Boykin, 1955; Damsgaard - Sorensen, 1946; Ghani and "Aleem, 1952 and Kaila, 1961). Results of a green house experiment at Ottawa (MaClean and Cook, 1955) showed that liming markedly increased the supply of available phosphorous in several acid soils.

The changes in phosphate sorption with pH in field experiment reported more than those where the pH was altered in the laboratory (Mishra and Ojha, 1970). Eid, Black and Kempthrone (1951) found that availability of soil phosphorous to plants depended on a fraction of the inorganic phosphorous at a soil temperature of 20^{0} and at a soil temperature 35^{o}C, however, the availability depended on a portion of organic phosphorous.

POTTASSIUM :

Limed soils have frequently been found to retain more potassium than acid soils (Mehlich, 1943; Thomas and Coleman, 1959). In an experiment with a spodosol A_p horizon with very high pH - dependent CEC, liming was found to depress the activity of solution potassium and induced lower K uptake by plants (Bartlett and McIntosh, 1969).

The effect of soil pH on potassium fixation has been investigated principally in connection with experiments on application of $CaCO_3$. In some instances liming has increased potassium fixation and in others it has had little effect. Kaila (1965) examined the pH effect in measurement of potassium fixation by a large number of soil samples from Finland and found a significant increase in fixation with an increase in soil pH. Ganje (1964) found that fixation of potassium under moist conditons by soils containing vermiculite type minerals was little influenced by pH in the range from 3 to 7 as long as the concentration of Al remained low. High concentration of non exchangeable interlayer Al resulting from the soils with dilute acid prevented fixation of potassium at pH 3. Fixation occured again when the acid treated soil were adjusted to pH 7.

Jasmin and Heeney (1962) observed that application of agricultural limestone in soil at 9 tons/Hectare reduced exchangeable potassium in soil. Macoleod et.al., (1964) found that with the increasing amount of dolomitic limestone, there was a decrease in exchangeable potassium. Tiwari et.al. (1971) observed that an increase in Ca/Mg ratio in nutrient solution decreases the K uptake by pea plant.

Margdoff and Bartlett (1980) showed that lime addition increases the pH and the solution potassium decreases. They also stated that the influence of lime on potassium availability could be even more severe. This effect has been explained as an opening up of K-selective exchange sites which were blocked by Al at low pH (Nemeth and Grimme, 1972) or as lowered percent K saturation caused by the increased CEC (Bartlett and McInthosh, 1969).

On the contary, many investigations have observed that liming of acid soils increased the K-uptake by plants. Thompson and Robertson (1969) observed that liming increased the extractable K in the soil. Goralaski and Mercik (1970) observed that clover showed an increase in K-uptake due to liming on acid soils (pH 5.2 to 5.5).

There are other reports also which show that liming does not influence the potassium uptake and availability in anyway. Mate et. al. (170) found no significant effect on phosphorous and potassium availability. Lutz (Jr) et.al., (1972) found no variation in potassium content of maize with liming rates.

Liming of acid soils may significantly decrease the loss of potassium by leaching. For example, shaw and Robinson (1960) found that the leaching of Potassium from loam soils in Tennersee was decreased from 58 Kg/hectare in the untreated control soil (pH = 4.5) to 9 Kg/hectare from the same soil after a heavy application of dolomitic limestone.

MICRONUTRIENTS

Lime additions to soils drastically modify the solubilities of number of the trace elements, leading to the alleviation of toxicities in some instances and to the production of deficiencies in others (Coleman et.al., 1957) Liming of a soil often affects the availability of heavy metals to plants (Smith, 1968; Singh, 1971; Maclean, 1970; Chaney et.al., 1977). It is reasonably well understood that the availability of all micronutrients except Mo decreases with pH. Soil pH has been identified as a particularly critical parameter in regulation of micronutrient availability. Brown and Holmes (1956) and Gupta et.al., (1969) reported that the solubilities and plant availabilities of copper, zinc and iron are generally believed to decrease when soils are limed. Pieve and Rinkis (1962) concluded that in slightly acid, neutral and alkaline soils Ca is antagonistic to Cu, Mn, Fe, Mg and P. Lutz et.al. (1972) observed a decrease in the concentration of Cu, Zn, Pb, Mo and Al in the maize, when soil pH was raised from 3.9 to 6.1 by liming. Sinha et.al., (1978) found that soil pH and organic matter content significantly affected the solubility of Fe, Cu, Mn and Zn cations. They expressed the solubility of Mn, Cu, and Zn as a function of soil solution pH. Maguire et.al. (1981) found that the amount of Cu and Zn sorbed increased with pH by soil clays. Datta and Gupta (1984) reported that application of pressmud and lime to ameliorate soil acidity resulted in significant reduction in the availability of zinc and iron in soil but not to the level of deficiency. Epstein and Stout (1951) found the solubilities of given doses of iron, Manganese and zinc in clay system to decrease sharply with the addition of $Ca(OH)_2$.

ZINC :

The decreasing trends of Zn in soils after liming was reported by wear (1956), Singh and Singh (1981) Adams et.al., (1982) and others. According to Teeper (1952) and Threne (1957), Ca^{++}ions released from liming mateials acts as strong absorbent of Zn, thus resulting in its fixation. Woltz et.al., (1953) reported that the application of limestone resulted in greater fixation of zinc in soil. Nair and Mehta (1959) found a significant correlation coefficient (r = 0.402) between pH and 0.1 N HCl soluble Zn content of Gujrat soils and observed in a number of instances the availability of Zn decreased as lime content increased.

The absorption of Zn by the soil can be influenced by pH, since field studies have shown that Zn is more available to plants under acid soil conditons than under basic soil conditions (Miller et.al., 1964). In laboratory experiments with clays (Bingham et.al., 1964; Jurinak and Bauer, 1956 and Reddy and Perkins, 1974). It has been determined that more Zn is adsorbed in basic than in acidic media. Chatterjee and Das (1964) found that there was more ammonium acetate extracted Zn in soil with pH below 6.0 and its content decreased as pH rose above 7.0. Gupta and Singh

(1972) recorded a significant correlation between $CaCO_3$ and available Zn content of Indore soils. On the other hand Udo et.al. (1970) found no significant correlation between Zn content and $CaCO_3$. Ganjir et.al., (1973) stated that higher values of available sinc could be attributed to the lower pH. Similarly Bandopadhya and Adhikari (1975) ovserved that application of lime and dolomite on acid alluvial soils decreased the availability of Zn. Maclean (1974) found that liming of an acid sandy loam soil (pH 4.9) to about neutral point reduced the amounts of extractable zinc markedly. Shuman (1975) reported increase in zinc adsorption with increasing soil pH particularly on coarser textured soils. Similar decrease in exchangeable zinc as pH increased were seen by Iyeneger et.al., (1981) and Sims and Partric (1978). MaCbridge and Blasiak (1979) observed increase in soil solution zinc at pH value 7.5, due to formation of soluble zinc organic matter complexes.

COPPER

Availability of copper in a soil depends upon the number of factors, of which pH, organic matter, total copper, calcium carbonate, soil texture are important ones. Frequently several factors are effective at the same time and it is not possible to single out contribution of each.

Gilbert (1952), in reviewing the role of copper in nutrition, concluded that though copper availability generally decreases on liming, the addition of lime to soils high in organic matter may result in bound copper to more available forms. Peech (1941) observed that copper and zinc added to a sandy soil were much less soluble at pH 6 than at pH 3.

Neelakantan and Mehta (1961); Agrawal and Motiramani (1966), Rai and Associates (1969), Grewal et.al., (1969); Bande et.al., (1973) and others observed a significant negative relationship between pH and amount of available copper in soils of Gujarat, Madhya Pradesh and Punjab respectively.

$CaCO_3$ has been reported to decrease the availability of copper by bringing about a change in soil reaction. Rai and Mishra (1967); Lal (1968); Grewal et.al. (1969); Mandal & Jha (1970) etc. observed a decrease in the amount of exchangeable copper with an increase in $CaCO_3$ content. Contrary to this, Lodha and Basar (1971) did not record any consistent relationship and Agrawal et.al., (1964) and Kavimandam et.al., (1964) observed a positive relationship between available copper content and pH of some tropical soils. Bandopadhya and Adhikari (1975) observed that application of lime and dolomite on acid alluvial soils did not affect the availability of copper. According to Sims (1986), soil pH had only minor effects on distribution of Cu. Mishra and Tiwari (1964) reported that the black soil retained a higher amount of applied copper in comparison to red and sandy loam ones because of its high organic matter content and higher pH values.

MaClaren et.al., (1973) found increased Cu adsorption over a pH range of 5 to 7. Availability of copper is dependent on soil pH but does not normally increase appreciably unless pH falls below 5.0.

Jarvis (1981) and Maclaren et.al., (1973, 1983) reported an increase in Cu sorption as pH increased primarily due to greater association with oxides. Kanwar (1954) found that the copper fixation in soils was associated with formation of organometallic compounds.

IRON :

The most readily available form of iron taken by plants from the soils is ferrous (Fe^{2+})ion, the availability of which is governed by several important factors such as soil reaction, texture, $CaCO_3$ content, organic matter and water logging. The factors influence redox potential and hydration and dehydration of iron compounds.

There is abundant evidence that there exists a definite relationship between Fe^{2+} content and pH of the soil. In general, the optimum pH for most plants is about 6.0 to 6.8. In this range, there is usually neither execess nor a deficincy of available iron.

Dhamija et.al. (1956), Hoshiar Singh (1964), Bhumbla et.al., (1969), Gupta et.al., (1969), Singh and Ram (1975) and others, found a negative relationship between pH and exhangeable and extractable iron in non-calcaerous soils. Liming significantly reduced the available Fe content in soils. Liming significantly reduced the available Fe content in soils and the adverse influence on Fe solubility was brought out by Gupta et.al., (1969). Lodha and Basar (1971) found a decrease in available Fe with an increase in pH in medium black and mixed red black soil of Rajasthan. Yadav and Singh (1983) studied the influence of applied Cu, Fe and $CaCO_3$ on DPTA extractable Cu and Fe in texturally different soils and found that application of lime (2% $CaCO_3$) decreased the DPTA extractable period. Gupta et.al. (1986) observed antagonistic effect of lime on Iron and Aluminium.

Thus we find that variations in critical soil chemical parametes such as pH, $CaCO_3$ etc. can induce shifts in micro nutrient pool, which may result in micronutrient deficiency in all cases but toxicity in Molybdenum with few reported exceptions.

CHAPTER - 3

METERIALS AND METHODS

MATERIALS AND METHODS

Soil samples used in this experimental work were collected from fallow land 3-4 km. away from Khetri copper complex. Soil samples were taken from 0 to 9 inches of the top soil. Grasses were the main vegetation. (TABLE - 3)

Tailings samples were collected from the tailings ponds at Khetri copper complex Rajasthan from upper 0-12 inches. Then the soil and tailings were air dried, powdered, sieved through a 2mm sieve.

For the purpose of studying the effect of liming on physio-chemical properties of soil-tailings mixture from Khetri copper complex area, Rajasthan. Soil and tailings were mixed in different proportions by weight and their lime requirements were determined. Soil and tailings were mixed in 25%, 33%, 50%, 66%, 75% and 100% tailings ratio.

Lime requirement of the soil - tailings mixtures and tailings :

The procedure given by shoemaker et. al. (1961) is being widely followed for determining lime requirement of acidic soil samples of pH less than 6.0. Khetri soil samples has pH 7.2 and tailing has pH 3.95 which gives pH of different mixtures ranging grom 4.14 to 4.96. So this procedure is satisfactory for concerned samples.

Insturment :

A glass electrode degital pH meter was used.

Reagents :

Extractant buffer : 1.8 gm P-nitro phenol, 2.5 ml triethanolamine, 3.0 gm potassium Chromate, 2.0 gm Calcium aceteate and 53.1 g Calcium chloride (all chemically pure) were dissolved in one litre of distilled water and the pH adjusted to 7.5 with dilute NaOH solution.

Procedure :

5 gm of air dried soil, tailings and soil-tailings mixtures were taken in a dry 50 ml beaker. To this 5 ml of doubled distilled water and 10 ml of the extractant buffer were added and stirred contineously for 10 minutes. The pH of the suspension was determined on the basis of which the requirement of lime was given in tons of pure calcium carbonate per acre required to bing the soil to pH indicated. (Table-1) These values were converted in gm of CaO/500 gm of soil samples to bring the samples to pH 7.

Table 1 : Amount of lime required to bring mineral soils to the indicated pH according to soil buffer pH.

Soil buffer pH	Agriculture ground limestone (tons/acre)[a]		
	7.0	6.5	6.0
6.8	1.4	1.2	1.0
6.7	2.4	2.1	1.7
6.6	3.4	2.9	2.4
6.5	4.5	3.8	3.1
6.4	5.5	4.7	4.5
6.3	6.5	5.5	4.5
6.2	7.5	6.4	5.2
6.1	8.6	7.2	5.9
6.0	9.6	8.1	6.6
5.9	10.6	9.0	8.0
5.8	11.7	9.8	8.7
5.7	12.7	10.7	9.4
5.6	13.7	11.6	10.2
5.5	14.8	12.5	10.9
5.4	15.8	13.4	11.6
5.3	16.9	14.2	12.3
5.2	17.9	15.1	13.0
5.1	19.0	16.0	13.7
5.0	20.0	16.9	13.7
4.9	21.1	17.8	14.4
4.8	22.1	18.6	15.1

Source : "Recommended chemical soil test procedures for the North Central Region" Bulletin No. 499, North Dakota Agricultural experiment station, North Dakota state university, Fargo, 1975.

a. To convert ton/acre to MT/Hectare, multiplied by 2.24.

Once the lime requirement in the form of gm of CaO/500 gm of samples was known, the lime was added to different soil tailings mixture. These different amount of lime were added to one particular soil-tailings mixture. Firstly, amount of lime being lime requirement. Secondly, half of the lime requirement and thirdly, Double, the lime requirement. This was done for all types of mixture of soil and tailings. It can be represented as follow.

A_1	B_1	C_1
100%T	100%T	100%T
A_2	B_2	C_2
75%T	75%T	75%T
A_3	B_3	C_3
66%T	66%T	66%T
A_4	B_4	C_4
50%T	50%T	50%T
A_5	B_5	C_5
33%T	33%T	33%T
A_6	B_6	C_6
25%T	25%T	25%T

Where A = half of the respective lime requirement for that particular mixture

B = Actual lime requirement in gm of CaO/500 gm for particular soil - tailings mixture

C = Double of the lime requirement in gm of CaO/500 gm of soil - tailings mixture.

Different ratios of soil tailings mixture were made on the weight basis. Samples were kept in one litre plastic beakers. After the addition of lime the soil - tailings mixtures were kept at 50% of their water holding capacity.

At the interval of 15 days, the mixture samples were taken out till 60 days. Mixture samples taken out at different intervals are dried, crushed and kept in polythene bags for analysis of various pysio-chemical parameters.

The parameters and anahytical methods for samples of soil, tailings and soil-failings mixtures are given in the following table:

Description of the procedure of analysis:-

i) pH : pH of the samples were measured by digital pH meter using 1 : 5 sample distilled water ratio.

ii) EC : This was measured by systronic conductivity meter using 1 : 5 samples water suspension.

iii) **Organic Carbon :**

Organic carbon was determined by the method of Walkley and Black in which the reducing material in soil is oxidised by chromic acid formed by addition of concentrated H_2SO_4 to potassium dichromate solution as described by Allison (1965),

Table 2

S. No.	Parameter	Procedure
1.	pH	Digital pH meter
2.	EC	Systronic conductivity meter
3.	Organic carbon	Titrimetric (Walkley and Black)
4.	Available Nitrogen	Subbiah and Aziza method (Titrmetric)
5.	Total Nitrogen	Titrimetric (micro kjeldahl method)
6.	Available phosphorous	Colorimetry Moly bednum Blue Colour method.
7.	Total phosphorous	Colorimetry (Perchloric - Nitric-sulphuric acid digestion, molybednum blue colour method.
8.	Available potassium	Flame photometer Ammonium acetate extraction method)
9.	Total potassium	Flame photometer (perchloric -Nitric - Sulphuric acid digestion)
10.	Heavy metals (total)	Atomic absorption spectorscopy (digestion)
11.	Available Heavy metals	DTPA (Diethylene Triamine penta acetic and) extraction A.A.S.

Principle:

Organic matter is oxidised by a known volume of acidified standerd potassium dichromate and the excess of dichromate is back titrated with N/2 terrous ammonium sulphate using diphenylamine as indicator.

Reagents:

(a) Standaard potassium dichromate (IN)

49.0 gm of $K_2 Cr_2O_7$ was dissolved in diistilled water and the volume made upto 1000 ml.

(b) Ferrous ammonium sulphate (N/2)

196 gm of $FeSO_4 (NH_4)_2 SO_4 \cdot 6H_2O$ was dissolved in distilled water, 15 ml of conc. H_2SO_4 was added and made upto 1000 ml with distilled water. This was standerised with standerd IN $K_2Cr_2O_7$ solution.

(c) Diphenylamine Indicator

0.5 gm oif reagent grade diphenyl amine was dissolved in 20 ml. of water and 100 ml of conc. H_2SO_4 was added and mixed slowly.

(d) 85% orthophosphoric acid

(e) Solid sodium fluouride (NaF)

Procedure :

2gm of soil sample was taken in 500 ml conical flask and exactly 10 ml of IN $K_2Cr_2O_7$ solution and about 20 ml of conc. H_2SO_4 were added to it. The mixture was allowed to stand for 30 minutes and then diluted to 200 ml with distilled water.

10 ml. of H_3PO_4, 0.2 gm of NaF and about 1.0 ml. of diphenylamine indicator were added and the solution was back titrated with N/2 Ferrous ammonium sulphate solution. The colour was dull green at the begining, then shifted to a turbid blue and at the end point changed sharply to brilliant green. A standerisation blank without soil was run simultaneously in the same way.

Calculation:

$$\% \text{ of organic carbon} = \frac{(a-b)\times 0.003\times N\times 100)}{W}$$

where

a = Blank titiration value

b = Sample titration value

N = strength of ferrous ammonium sulphate

W = Weight of soil

(iv) **AVAILABLE NITROGEN OR MINERALIZABLE NITROGEN** (Alkaline permangnate method)

(Subbiah and Asija, 1956)

Principle :

Soil on digestion with alkaline Permangnate solution releases ammonia, both from the inorganic ammonium compounds and organic nitrogen pool by a process of oxidation and hydrolysis. The determination of ammonia liberated serves as an index of the available/mineralizable nitrogen status.

Reagents :

i) Sodium hydroxide solution (2.5%)

25 gram of NaoH dissolved in 1 litre of distilled water.

ii) 0.32% Potassium permangnate solution ($KMnO_4$)

3.2 gram of $KMnO_4$ was dissolved in 1 litre of distilled waters.

iii) 0.02N NaOH (sodium hydroxide).

The solution was standerised by titrating against standerd oxalic acid.

iv) 0.02N Sulphuric acid (H_2SO_4).

It was preapred by titrating against standard NaOH solution.

v) Methyl red Indicator

0.1 gm of reagent was dissolved in mixture of 60 ml ethyl alchohal and 40 ml water and mixed well.

Procedure :

10 gram of soil sample was taken in 500 ml dry kjeldahl flask. To this 10 ml of distilled water was added followed by 50 ml of each 0.32% $KMnO_4$ solution and 2.5% NaOH solution. The contents of the flask were distilled and about 75 ml of distillate was collected at a steady rate in a 10 ml standerd sulperic acid (0.02N) with methyl red indicator. The bumping during distillation was prevented by adding few glass beads. Nearly 75 ml of distillate was collected in about 30 minutes. Ammonia released during the reaction, reacted with standerd H_2SO_4 which was back titrated against standerd (0.02N) NaOH using methyl red indicator which turned from red to pale yellow colour at the end point. A blank was also run simultaneously.

Calculation :

1 ml of 0.02N sulphuric acid = 0.28 mg of N therefore PPm of

$$\text{Available Nitrogen} = \frac{(a-b) \times 0.28 \times 1000}{C}$$

where a = Blank titration value with 0.02N NaoH

b = Sample titration value with 0.02N NaOH

c = Weight of soil in gm.

(V) TOTAL NITROGEN

Principle :

Soil sample on digestion with concentrated sulphuric acid and some catalyst and followed by steam distillation releases ammonia. Determination of this ammonia liberated gives total nitrogen in the soil sample.

Reagents :

(a) Sulphuric acid (H_2SO_4), concentrated

(b) Digestion mixture:

10 parts of regent grade potassium sulphate and 1 parts of $CuSO_4$ grinded seperately to fine powder and were mixed with 0.1 parts of Se power.

(c) Standard sulphuric acid (0.05N)

(d) Mixed indicator solution :

0.5 gram of bromocresol green and 0.1 gm of methyl red was dissolved in 100 ml of 95% ethanol and solution was adjusted to the bluish purple colour at pH 4.5 with dilute NaOH or HCl.

(e) Boric acid solution:

Approximately 40 gm of Boric acid (H_3BO_3) was dissolved in one litre of distilled water containining 5 ml of mixed indicator.

(f) 50% of NaOH solution.

Procedure:

2 gms of soil sample was taken in a dry macro-kjeldahl flask and 20 ml of water was added. Flask was swirled for a few minutes and allowed to stand for 30 minutes. Then 20 grams of digestion mixture was added followed by 35 ml of concentrated sulphuric acid. The content was treated slowly on the digestion stand till the forthing had ceased and then heated strongly till the mass appeared bluish green. The content was cooled and about 25 ml of distilled water was added slowly and with shaking to the flask. The flask was swirled and allowed to stand till the contents were cold. The digested material was transferred with two or three washing into the vaccum mentle of the steam distillation unit. 30-35 ml. of 50% NaOH was added and steam distillation was carried out for about 5-7 minutes. The distillate containing ammonia was collected into 10 ml. of Boric acid solution. The resulting ammonia borate (green colour) was titrated against 0.05 NH_2SO_4 to a pink colour end point.

Calculation :

$$N \% \text{ in soil} = \frac{N.V.\ 100 \times 0.014}{W}$$

$$= \frac{1.4\ NV}{W}$$

where

N = Strength of H_2SO_4 in terms of normality (0.05N)

V = ml of 0.05N H_2SO_4 required for titration

W = Weight of soil in grams.

(VI) AVAILABLE PHOSPHOROUS :

Available phosphorous was determined by colorimetric method using the sensitive "Molybdenum blue colour method" with L- Ascorbic acid as the reductant.

Principle :

This method is based on the formation of hetrophosphomolybdate compound when an acid molybdate is added to solution containing ortho-phosphate. Reduction of this complex gives the chracteristic mohybdenum blue colour. The intensity of the blue colour is proportional to the phosphate concentration.

A colorimeter is used to measure the intensity of the blue colour.

Instrument:

U - V -260 spectrophotometer

Make - Shimadzu

Wavelength used - 882 nm.

Method :

The method selected for determination of phosphorous was proposed by John (1970).

Regents :

(a) Bray and Kurtz No.1 solution (0.03 NH_4F in 0.0225 HCl was used as extractant for available phosphorous. This was prepared by dissolving 1.11 gram of ammonium flouride in one litre of 0.025 HCl.

(b) Standerd phosphate solution: 0.2195 grams of potassium dihydrogen phoshate dried at 40^oC was dissolved in distilled water and volume was made upto one litre to give a stock solution containing 50 ppm of phosphorous. From this standerd solutions of varying concentrations of phosphorous were prepared when required.

(c) Stock solution: 20 gms of ammonium molybdate was dissolved in about 300 ml of distilled water. Then 450 ml of 10N sulphuric acid was added with stirring. To this, 10 ml of antimony potassium tartarate was added. This was diluted to one litre with distilled water and stored away from direct sunlight.

(d) Mixed reagent : Mixed reagent was prepared by adding 1.5 gram of L- ascorbic acid to 100 ml of stock solution.

Procedure :

2 gram of dry soil was shaken with 20 ml of extractant (Bray and Kurtz No.1 solution) for one minute, filtered immediately through whatman No.42 filter paper. 5 ml of this clear filterate was diluted to 20 ml in a 25 ml volumetric flask, then 2.5 ml of mixed reagent was added and the volume was made upto the mark.

For standerd curves, 5 ml of standerds varying from 0.1 to 1 ppm were transferred to 25 ml volumetric flask, 2.5 ml of mixed reagent was added and volume was made upto the mark.

First the standerd phosphorous solutions were fed into UV-260 speetrophotometer and the standerd curves was obtained using 882 nm wavelength with reference to distilled water. Following this, the soil sample extracts were inserted with respect to Bray and Kurtz solution No.1 and corresponding concentrations were obtained. All measurements were made between 30-60 minutes after the addition of mixed reagent.

Calculation :

P in ppm = P in solution X Dilution times.

Digestion of samples for total phosphorous, total potassium and heavy metals:

Perchloric - Nitric- sulphuric acid digestion was used for total phosphorous, total potassium and total heavy metals. Reagent :

1. Perchloric acid 60% (AR)
2. Concentrated nitric acid
3. Concerntrated sulphuric acid (A.R.)

Procedure :

0.5 gm of soil sample was weighed and transferred to 300 ml conical flask. 2 ml of concentrated sulphuric acid was added and watch glass was kept on the mouth and mixture was heated up till fumes ceased. Then 20 ml of 1:3 mixture of 60% Perchloric concentrated nitric acid acid was added and digestion was carried out for 5 hours on a hot plate untill the solution appeared colourless clear. If not, more concerntrated HNO_3 was added and continued digestion till clear solution. The digested solution was diluted and filtered through whatman No.42 filter paper. The residue was washed by distilled water. The filtrate was made upto 100 ml in volumetric flask with distilled water and stored in plastic bottles.

viii) **Availble Potassium :**

The term available potassium incorporates both exchangeable and water soluble torms of the nutrient Present in the soil is extrected with neutral ammonium acctate the potassium concentration can be measured by flame photometer using the appropriate standards

For the present study the neutral IN ammonium accetate extraction method was used and K was measured by flame photometer.

Reagents :

i) Extractant IN Ammonium accetate (pH 7) :

57.5 ml glacial acetic acid and 60.0 ml of concentrated ammonia solution were added in 30 ml of water and mixed well. The soultion was diluted to 1 litre and mixed thoroughly. The pH of the solution was adjusted to $7.00 \pm .005$ with drops of acetc acid or ammonia as necessary.

(ii) Potassium standard :

1.907 gram of kCl dried at $110^{0}C$ was dissolved and diluted to 1000 ml with distilled water. From this suitable working standards were prepared.

Procedure :

Extractoin of soil with neutral amonium accetate:

4 gm of air dried sieved soil was taken in 500 ml conical flask and 100ml of IN ammonium accetate soultion was added to it. The mixture was shaken for one hour on a roating shaker. The mixture was filtered through No. 41 filter paper into Polythene bottles and first 20 to 25 ml filterate was rejected.

Measurement of K concentration by flame photometer:

The potassium filter was selected. The gas pressure, slit width and other settings were adjusted as required.

A caliberation curve was drawn from the standard range by setting the top standerd to a suitable scale deflection and the zero ppm standerd to zero. The operation was repeated with both the caliberation standerds a sufficient number of times to secure a reliable average reading for each solution.

The sample solutions and blanks were aspirated into the flame under the same condition as the standards. The top, zero and an intermediate standerds were frequently checked. The calibration curves was used to determine the exact concentration of K in the sample solutions.

K (ppm) = K in portion (ppm) X D

D = Dilution times.

vii) Total phosphorous :

5 ml of digested solution was taken and 2.5 ml of mixed reagent was added to it and the volume was made upto 25 ml with distilled water in volumetric flask. The absorbance was measured at 882 nm in similar manner as in the case of available phsophorous.

Calculation :

PPm of phosphorous = phosphorous in solution (PPm) x Dilution times.

ix) Total potassium :

It was determined from digested solution by digital flame photometer in similar manner as in the case of available phosphorous.

Calculation :

K conc. in PPm = K in solution (PPm) x dilution times.

viii) AVAILABLE HEAVEY METALS (Cu, Zn and Fe)

Several reagents have been employed from time to time for the extraction of available micro-nutrients in the soil out of which DTPA (Diethylene Triamine Penta acetic acid) appears as quite promising having wider appplicability. Cu, Zn and Fe were estimated in a single extraction with DTPA by setting the instrument for each of them and using the respective standerd curve.

Instrument :

Atomic Absorption spectrophotometer (AAS)

Regents:

i) DTPA (Diethylene triamine penta acetic acid) 0.005M solution

ii) TEA (Triethanolamine) 0.1M (AR)

iii) $CaCl_2$ $2H_2O$ (AR), o.1M solution

The extracting reagent was prepared by taking 1.967 gm of DTPA and 1.470 gm CARL2 - 2hZO in a beaker. To this 20 to 25 ml of doubled distilled water was added and 13.3 ml of TEA followed by 100 ml of double distilled water. This was transferred to one litre volumetric flask and the volume was made upto the mark with distilled water. The pH of the solution was adjusted to 7.3 with dilute HCl.

Procedure for extraction :

10 g of soil was taken in 100 ml conical flask, to this 20 ml DTPA was added and was shaken for 2 hours. The extract was filtered through whatman No. 42 and Zn, Cu and Fe was estimated with AAS.

Procedure for standerd curve :

(a) Zinc

One gram of pure Zn metal was dissolved completely in minimum amount of dilute HCl and volume was made upto one litre with double distilled water and then transferred to plastic bottles. This stock solution contains 1000 g Zn/ml. A working standrerd of 25 Mg/ml was prepared by diluting 2.5 ml of the stock soultion to 100 ml.

In six volumetric flasks, required aliquots were taken and standerds of 0,0.5,1.0,1.5,2.0 and 2.5 PPm Zn solution were made and the standard curve was prepared against the readings of the AAS after necessary setting and caliberation of the instrument.

(b) Copper

A stock solution of 1000 PPm Cu was obtained by dissolving exactly one gram of the pure (AR grade) metal in 50 ml. of dilute (1.1) HNO_3 and finally diluting to 1000 ml with doubled distilled water. From this, working solutions were prepared.

(c) Iron

Exactly 1g of AR grade Fe metal was dissolved in 50 ml of dilute HNO_3 and volume was made to one litre with double distilled water to get stock solution of 1000 PPm. From this working solutions were prepared.

Calculation:

Heavy metal concentration in PPm

= Heavy metal concentration in solution X dilution factor.

Total metals :

Total metals were measured in the same way from digested soil solution by AAS.

TABLE 3

PROPERTIES OF SOIL AND TAILINGS

PARAMETERS	SOIL	TAILINGS
pH	7.12	3.95
EC	127.4 μmhos/cm	2.88 mmhos/cm
Organic Carbon	0.176%	0.83%
N (Available)	72 ppm	23.6 ppm
N (Total)	0.098%	0.021%
PO_4 (Available)	16.36 ppm	1.2 ppm
PO_4 (Total)	296 ppm	225 ppm
K (Available)	110 ppm	25 ppm
K (Total)	1780 ppm	1700 ppm
Fe (Total)	0.02956%	0.1494%
Cu (Total)	160 ppm	1560 ppm
Zn (Total)	57.6 ppm	120 ppm
Fe (Available)	25.6 ppm	212.8 ppm
Cu (Available)	8.8 ppm	183.8 ppm
Zn (Available)	2 ppm	14 ppm

CHAPTER - 4

EXPERIMENTAL RESULTS

Table 4 : Periodic changes in pH of soil-tailings mixtures and tailings due to liming

Time (Days) Soil tailings mixtures*	0	15	30	45	60
25A	4.96	5.6	5.3	5.1	5.0
25B		6.5	6.3	6.2	6.1
25C		7.2	7.1	7.0	7.0
33A	4.79	5.4	5.2	5.1	5.0
33B		6.6	6.2	6.1	6.1
33C		7.4	7.2	7.2	7.1
50A	4.39	5.6	5.4	5.3	5.2
50B		6.9	6.5	6.3	6.2
50C		7.7	7.2	7.0	6.9
66A	4.30	5.5	5.4	5.3	5.2
66B		7.1	7.3	7.2	7.0
66C		7.5	7.4	7.2	7.1
75A	4.14	5.5	5.6	5.3	5.2
75B		6.8	7.1	7.0	7.2
75C		7.6	7.4	7.4	7.3
100A	3.95	5.9	5.6	5.5	5.4
100B		6.7	7.0	6.8	6.8
100C		7.3	7.1	6.9	6.8

* A = Amount of Lime half of Lime requirement

B = Corresponding to lime requirement

and C = Double of the Lime requirement

Table 5 : Periodic changes in alectrical conductivity (m mhos/cm) of soil-tailings mixtures and tailings due to liming.

Time (Days) ----------- Soil tailings mixtures*	0	15	30	45	60
25A	1.165	1.086	1.608	2.05	1.804
25B		1.064	1.587	2.01	1.834
25C		1.35	1.458	2.11	1.889
33A	1.115	1.296	1.785	2.32	2.17
33B		1.202	1.922	2.45	2.30
33C		1.546	2.01	2.39	2.33
50A	2.21	2.12	2.1	2.86	2.30
50B		2.06	2.28	2.94	2.73
50C		2.03	2.32	3.02	3.0
66A	3.05	2.05	2.61	3.04	2.78
66B		2.09	2.39	2.99	2.95
66C		2.11	2.77	3.3	2.93
75A	2.73	2.13	2.63	3.44	2.93
75B		2.47	2.6	3.36	3.28
75C		2.24	3.14	2.83	3.1
100A	2.88	2.44	3.11	3.6	3.15
100B		2.62	2.95	4.03	3.54
100C		2.78	3.46	3.05	3.03

* A = Amount of Lime half of Lime requirement

B = Corresponding to lime requirement

and C = Double of the Lime requirement

Table 6 : Periodic changes in Organic Carbon (%) of soil-tailings mixtures and tailings due to liming.

Time (Days) / Soil tailings mixtures*	0	15	30	45	60
25A	0.264	0.249	0.204	0.190	0.190
25B		0.249	0.219	0.204	0.204
25C		0.249	0.225	0.226	0.226
33A	0.278	0.264	0.235	0.219	0.196
33B		0.249	0.226	0.219	0.204
33C		0.235	0.235	0.23	0.23
50A	0.382	0.31	0.289	0.274	0.259
50B		0.31	0.297	0.281	0.266
50C		0.31	0.304	0.281	0.294
66A	0.454	0.348	0.327	0.312	0.304
66B		0.346	0.335	0.312	0.308
66C		0.341	0.335	0.327	0.327
75A	0.573	0.381	0.361	0.358	0.3543
75B		0.375	0.365	0.3543	0.3543
75C		0.371	0.369	0.358	0.3543
100A	0.83	0.389	0.361	0.342	0.339
100B		0.392	0.358	0.339	0.331
100C		0.367	0.3543	0.335	0.327

* A = Amount of Lime half of Lime requirement

B = Corresponding to lime requirement

and C = Double of the Lime requirement

Table 7 : Periodic changes in total Nitrogen content (%) of soil-tailings mixtures and tailings due to liming.

Time (Days) Soil tailings mixtures*	0	15	30	45	60
25A	0.077	0.075	0.075	0.075	0.073
25B		0.073	0.073	0.07	0.068
25C		0.07	0.068	0.066	0.063
33A	0.071	0.07	0.07	0.07	0.064
33B		0.07	0.068	0.068	0.064
33C		0.068	0.066	0.066	0.063
50A	0.057	0.057	0.057	0.057	0.054
50B		0.055	0.055	0.054	0.052
50C		0.054	0.054	0.05	0.049
66A	0.045	0.045	0.045	0.043	0.042
66B		0.045	0.045	0.043	0.042
66C		0.042	0.04	0.04	0.038
75A	0.04	0.04	0.04	0.04	0.038
75B		0.038	0.038	0.036	0.036
75C		0.038	0.038	0.036	0.033
100A	0.021	0.021	0.021	0.021	0.019
100B		0.021	0.021	0.021	0.017
100C		0.019	0.019	0.019	0.015

* A = Amount of Lime half of Lime requirement

B = Corresponding to lime requirement

and C = Double of the Lime requirement

Table 8 : Periodic changes in total phosphorous (ppm) of soil-tailings mixtures and tailings due to liming.

Time (Days) / Soil tailings mixtures*	0	15	30	45	60
25A	278	278	277	276	274
25B		277	275	274	272
25C		278	277	275	274
33A	270	269	269	268	267
33B		270	268	266	265
33C		270	268	267	265
50A	261	261	258	258	256
50B		260	258	257	255
50C		261	260	259	257
66A	245	245	244	244	243
66B		243	242	242	241
66C		244	244	243	243
75A	242	242	242	241	241
75B		241	241	241	239
75C		241	241	240	240
100A	225	225	224	224	224
100B		225	223	223	222
100C		225	225	225	224

* A = Amount of Lime half of Lime requirement

B = Corresponding to lime requirement

and C = Double of the Lime requirement

Table 9 : Periodic changes in total potassium (ppm) of soil-tailings mixtures and tailings due to liming.

Time (Days) Soil tailings mixtures*	0	15	30	45	60
25A		1760	1760	1760	1760
25B	1760	1750	1760	1760	1760
25C		1760	1760	1760	1760
33A		1750	1760	1750	1750
33B	1750	1750	1760	1760	1760
33C		1750	1750	1760	1760
50A		1740	1750	1750	1750
50B	1740	1740	1740	1740	1740
50C		1740	1740	1750	1750
66A		1720	1720	1710	1710
66B	1720	1740	1720	1710	1710
66C		1720	1720	1720	1720
75A		1720	1730	1720	1720
75B	1720	1730	1720	1720	1720
75C		1720	1720	1720	1720
100A		1710	1700	1700	1700
100B	1700	1700	1700	1700	1700
100C		1700	1690	1700	1700

* A = Amount of Lime half of Lime requirement

B = Corresponding to lime requirement

and C = Double of the Lime requirement

Table 10 : Periodic changes in Available nitrogen (ppm) of soil-tailings mixtures and tailings due to liming.

Time (Days) / Soil tailings mixtures*	0	15	30	45	60
25A	46.2	60.2	61.6	60.2	58.8
25B		65.8	65.8	67.2	68.6
25C		67.2	68.6	70.0	70.0
33A	37.8	42	42	43.4	43.4
33B		47.6	49	50.4	51.8
33C		49	53.2	54.6	57.4
50A	30.3	35	36.4	37.8	37.8
50B		39.2	39.2	40.8	42
50C		42	42	42	43.4
66A	26.6	32.2	33.6	33.6	35
66B		37.8	42	43.4	43.4
66C		39.2	42	43.4	43.4
75A	19.6	25.2	28	29.4	29.4
75B		30.3	33.6	35.0	36.4
75C		30.3	33.6	36.4	36.4
100A	23.8	30.8	33.6	33.6	33.6
100B		33.6	37.8	37.8	39.2
100C		35	37.8	37.8	37.8

* A = Amount of Lime half of Lime requirement

B = Corresponding to lime requirement

and C = Double of the Lime requirement

Table 11 : Periodic changes in Available phosphorous (ppm) of soil-tailings mixtures and tailings due to liming.

Time (Days) Soil tailings mixtures*	0	15	30	45	60
25A	2.1	2.65	2.85	2.6	2.5
25B		3.75	3.43	3.23	3.08
25C		4.2	3.9	3.75	3.78
33A	2.5	2.78	2.95	2.75	2.92
33B		3.25	3.28	3.07	2.75
33C		3.93	3.98	3.76	3.59
50A	1.6	2.09	2.27	2.13	2.25
50B		2.41	2.55	2.49	2.25
50C		3.2	2.78	2.6	2.65
66A	1.32	1.64	1.6	1.6	1.56
66B		2.13	2.22	2.25	2.2
66C		2.55	2.39	2.4	2.36
75A	1.25	1.56	1.75	1.78	1.8
75B		1.92	2.25	2.37	2.49
75C		2.32	2.48	2.52	2.56
100A	1.2	1.41	1.63	1.75	1.82
100B		1.58	2.16	1.9	1.78
100C		2.2	2.1	1.99	1.99

* A = Amount of Lime half of Lime requirement

B = Corresponding to lime requirement

and C = Double of the Lime requirement

Table 12 : Periodic changes in Available potassium (ppm) of soil-tailings mixtures and tailings due to liming.

Time (Days) / Soil tailings mixtures*	0	15	30	45	60
25A		43	46	52	57
25B	68	35	36	36	38
25C		43	43	40	40
33A		42	46	50	53
33B	63	35	38	35	35
33C		40	39	38	37
50A		35	38	40	45
50B	55	34	33	33	34
50C		40	35	32	33
66A		30	31	33	35
66B	40	30	32	30	30
66C		33	32	32	31
75A		20	18	22	22
75B	34	20	25	25	26
75C		27	24	25	23
100A		17	15	16	19
100B	25	18	22	20	23
100C		20	19	17	17

* A = Amount of Lime half of Lime requirement

B = Corresponding to lime requirement

and C = Double of the Lime requirement

Table 13 : Periodic changes in Available copper (ppm) of soil-tailings mixtures and tailings due to liming.

Time (Days) Soil tailings mixtures*	0	15	30	45	60
25A	56.8	40.4	46.2	48.4	51
25B		25.6	22	23	23
25C		20.6	19.2	21	24
33A	79.8	52.2	54.6	55	55
33B		28	28.4	30.2	28.2
33C		20.2	22	25.6	20
50A	109.6	68	72.4	66.2	60.8
50B		35	39	38	36
50C		25.4	30.6	27.8	24.4
66A	132.9	70	65	65	70.4
66B		32.4	33	33	30.4
66C		26.4	30.4	31	30
75A	137	50.2	43	40.6	40.8
75B		14.2	20.4	15	15
75C		21.02	21	19	19
100A	183	65.8	57	50.2	50.8
100B		23	20.6	20.6	18.8
100C		28.4	23	20.8	23

* A = Amount of Lime half of Lime requirement

B = Corresponding to lime requirement

and C = Double of the Lime requirement

Table 14 : Periodic changes in Available Zinc (ppm) of soil-tailings mixtures and tailings due to liming.

Time (Days) / Soil tailings mixtures*	0	15	30	45	60
25A	6	5	5	5.5	5.6
25B		3	2.8	3.2	3.2
25C		3	2.5	3	2.8
33A	4	4	4.8	4.5	5.2
33B		3	4	4	4.5
33C		2	2	3	3.2
50A	10	6.2	5.5	5.5	5.8
50B		4	4.7	4.9	5
50C		2	3.2	3	3
66A	10	6	5.8	5.5	5.9
66B		3	2.4	2.7	2.5
66C		2.5	2.8	3.1	3.3
75A	10	4	3.5	4	3.8
75B		2	2	2.5	3
75C		2	2	2	2
100A	14	4	3.6	4	4.2
100B		2	2.4	3	2.5
100C		2	2	2.5	2.5

* A = Amount of Lime half of Lime requirement

B = Corresponding to lime requirement

and C = Double of the Lime requirement

Table 15 : Periodic changes in Available Iron (ppm) of soil-tailings mixtures and tailings due to liming.

Time (Days) Soil tailings mixtures*	0	15	30	45	60
25A		74.5	82.4	77.8	78.6
25B	90.8	45.4	46	48.6	46
25C		40.2	40.2	42	45.4
33A		78	77.5	80.6	80.4
33B	103.4	55	57	60	57
33C		52.4	50.2	50.8	48
50A		68	65	65	68
50B	132.4	40	41	39	40
50C		27	30	35	33
66A		79.6	80.2	70.4	74.4
66B	153	39	35	40.8	40.6
66C		30.4	36.2	30	25
75A		84.6	75.2	78.4	78.2
75B	180.2	45.6	38	30.4	25
75C		34.8	35	29.6	20.4
100A		50.6	48.8	45.4	43
100B	212.8	45.6	35.4	30.2	24.5
100C		39	31	28	24

* A = Amount of Lime half of Lime requirement

B = Corresponding to lime requirement

and C = Double of the Lime requirement

Table 16 : Correlation Coefficients between pH and Available Nitrogen of different soil - tailings mixtures and tailings.

% of tailings	Correlation Coefficients	Regration equation
25	0.8196	Y = 23.88 + 6.575 X
33	0.8689	Y = 14.201 + 5.5321 X
50	0.8529	Y = 18.957 + 3.244 X
66	0.9173	Y = 8.7146 + 4.578 X
75	0.858	Y = 6.6466 + 3.796 X
100	0.8891	Y = 11.2383 + 3.7581 X

Table 17 : Correlation Coefficients between pH and Available Phosphorous of different soil - tailings mixtures and tailings.

% of tailings	Correlation Coefficients	Regration equation
25	0.9619	Y = 7.42 X - 1.307
33	0.9191	Y = 0.1917 + 0.4939 X
50	0.9043	Y = 0.13 + 0.3633 X
66	0.979	Y = 0.3648 X - 0.3263
75	0.9385	Y = 0.3570X - 0.2314
100	0.8347	Y = 0.232 + 0.2516 X

Table 18 : Correlation Coefficients between pH and Available Potassium of different soil - tailings mixtures and tailings.

% of tailings	Correlation Coefficients	Regration equation
25	-0.6817	Y = 91.84 - 7.7835 X
33	-0.7454	Y = 84.693 - 6.9542 X
50	-0.68206	Y = 65.987 - 4.6015 X
66	-0.6168	Y = 42.226 - 1.556 X
75	-0.0847	Y = 25.869 - 0.3029 X
100	-0.11298	Y = 21.165 - 0.333 X

Table 19 : Correlation Coefficients between pH and Available Copper of different soil - tailings mixtures and tailings.

% of tailings	Correlation Coefficients	Regration equation
25	-0.927	Y = 126.35 - 15.417 X
33	-0.21375	Y = 41.068 - 0.2573 X
50	-0.6117	Y = 1279.8 - 186.42 X
66	-0.2228	Y = 54.236 - 0.37 X
75	-0.2089	Y = 78.144 - 0.9 X
100	-0.8969	Y =301.19 - 40.88 X

Table 20 : Correlation Coefficients between pH and Available Zinc of different soil - tailings mixtures and tailings.

% of tailings	Correlation Coefficients	Regration equation
25	-0.9293	Y = 12.666 - 1.439 X
33	-0.8562	Y = 9.4765 - 0.9494 X
50	-0.9296	Y = 16.803 - 1.9275 X
66	-0.9559	Y = 16.825 - 1.9548 X
75	-0.8444	Y = 13.838 - 1.6411 X
100	-0.8541	Y = 21.68 - 2.7666 X

Table 21 : Correlation Coefficients between pH and Available Iron of different soil - tailings mixtures and tailings.

% of tailings	Correlation Coefficients	Regration equation
25	-0.9329	$Y = 187.858 - 21.249 X$
33	-0.9215	$Y = 169.12 - 17.076 X$
50	-0.895	$Y = 216.64 - 26.46 X$
66	-0.9227	$Y = 247.22 - 29.707 X$
75	-0.9198	$Y = 286.05 - 35.472 X$
100	-0.870	$Y = 126.99 - 12.88 X$

CHAPTER - 5

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

The results of the present investigation have been incorporated in this chapter under two different sections. The first section deals with the characteristics of experimental soil and tailings used and the second one represents the physio-chemical changes due to lime application on soil-tailings mixtures and tailings.

The analysis of different physical and chemical parameters of the lime applied soil - tailings mixtures for 60 days have been presented in different tables (3 to 14).

Properties of the soil employed in the experiment :

The soil samples used in the present investigation have been discribed in material and methods and are recorded in table-3. The pH of the soil was 7.12 (neutral) and electrical conductivity of the saturation extract was found to be 127.4 mhos/cm. The analysis indicated that the soil contained 72 ppm of available N, 16.36ppm of available potassium. The organic carbon of the soil was 0.176%. The concentrations of various heavy metals are also shown in table-3.

Properties of Tailings Used in the Experiment:

The general description about the tailings has been given in the materials and methods (table-3). The pH of tailings was found to be 3.95 (highly acidic) and the EC value was recorded to be 2.88m mhos/cm. The organic carbon content of the tailings was 0.83% which was considered to be higher. The analysis showed that tailings contained 23.6 ppm of available nitrogen, 1.2ppm of available phosphorous and 25ppm of available potassium. The Iron content of tailings was very high (0.1494%) and contents of other metals are given in table-3.

Effects of the application of various doses of lime on the different soil-tailings mixtures and tailings:

The experiments covering the lime application have been discribed in the materials and methods. Our aim and objectives were to find out the periodic changes that took place during the time period of 60 days. The different doses of lime include:

i) half of the lime requirement (A)
ii) lime requirement (B)
iii) Double of the lime requirement (C).

The lime soil: tailings propertions include 25%, 33%, 50%, 66%, 75%, and 100% (in terms of tailings %).

All the experiments were conducted at 50% water holding capacity of the corresponding soil-tailings mixtures and tailings at room temperature. The samples were collected regularly at the internal of 15 days. The detailed discussions on individual parameters viz. pH, EC etc. are to be followed:

pH

Periodic changes in pH of different soil-tailings mixtures with three doses of lime additions i.e., half of lime requirement (A), lime requirement (B) and double of the lime requirements (C) at time intervals of 15, 30,45, and 60 days are shown in table-4 and Fig. 5. Application of lime resulted in raising the pH for all doses of lime additions and for all soil-tailings mixtures, but the pH value were found to be less than the expected after different amount of lime additions except in the case of 50C and 66B, where increase in pH due to lime was appropriate.

From 15 day to 60 days pH of all soil-tailings mixtures for all doses of lime additions showed dcreasing trends with few irregularities. The decrease in pH from 15 days to 60 days after liming varried by 0.8 to 0.1 unit, but in most

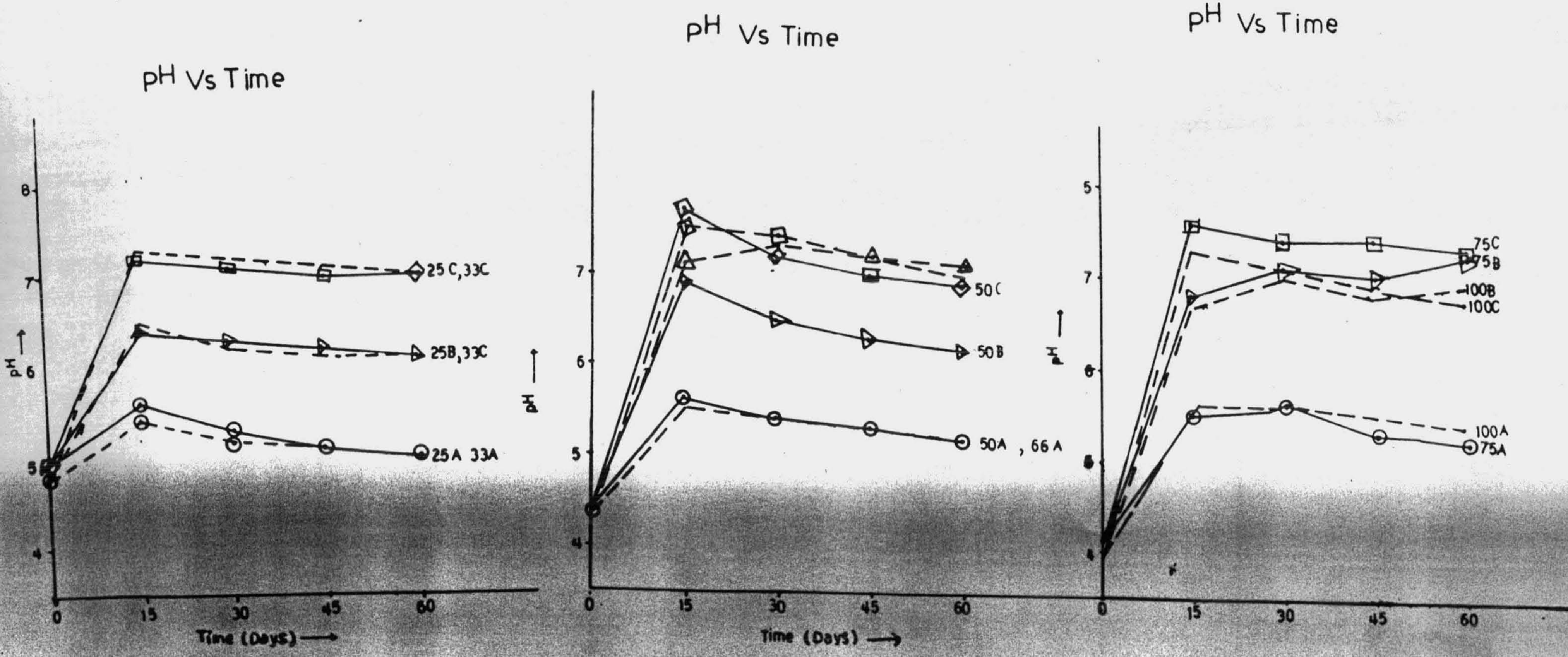


Fig. 1. Periodic changes in pH of different S-T mixtures and tailings due to liming.

cases it varried between 0.3 to 0.5 units. However, mixtures high in tailings percentage showed decreasing pattern after 30 days of liming instead of 15 days. In the case of 25A and 33A pH after 60 days was almost equal and near to the control pH respectively.

From the Fig. 1. it is evident that decrease in pH in soil-tailings mixtures, high in soil percentage was similar and uniform, but varied decreasing trends plus irregularities were found in high tailings percentage mixtures. The other important changes in pH could be observed from Fig. 1, so that for high tailings percentage mixtures, curves for B and C lime additions were very close to each other, but far above from that of A lime addition.

All the observed periodic variations may be explained by taking into consideration, the fact that tailings obtained from copper mining and ore processing contained sulfides of various heavy metals, which released sulfuric acid due to oxidation of these sulfides to sulfates (Pulford etal., 1983, Dave et.al., 1985 and Ivarson, 1973). So, we can say that oxidative dissolution of sulfide minerals is commonly associated with an increasing acidification of surrounding medium. So predicted lime requirements were found to be less than the actual required.

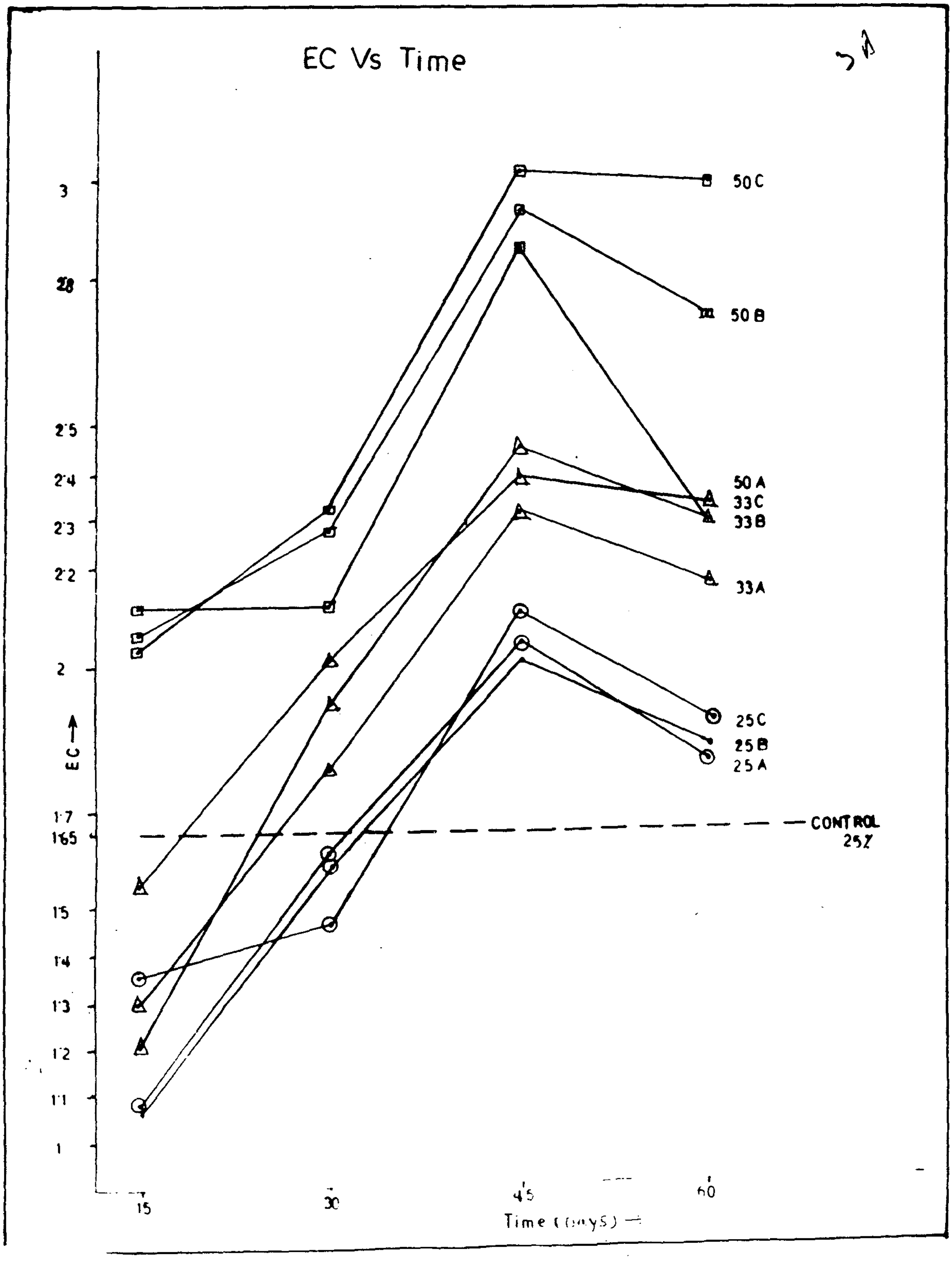


Fig. 2. Periodic changes in EC (m. mhos) of 25%, 33% and 50% S-T mixtures due to liming.

Other observations of changes in pH, irregularities in trends and also marked difference in the uniformity of trends between mixtures high in soil percentage and those of tailings percentage, may be attributed to the fact that tailings do not have the buffering capacity as soils and tailings represent extremely complex and variable environment (kelly and Tuovinen, 1988). So a relatively small change in lime addition on soil- tailings mixtures high in tailings percentage, can change a number of variables which controls pH and hence fluctuations and irregularities cannot be overrulled.

Irregularities in pH variations of various soil-tailings mixtures following liming can be correlated with the findings of Smith (1930), who reported that copper - bearing pyrites oxidized at widely different rates depending upon the source and other factors.

EC

Periodic changes in EC of different soil-tailings mixtures with different lime addition (A, B and C) at time intervals of 15, 30, 45 and 60 days are shown in table-5 and Fig.2,3 & 4. Application of lime resulted in the decrease of EC after first 15 days following liming for all mixtures and

3B

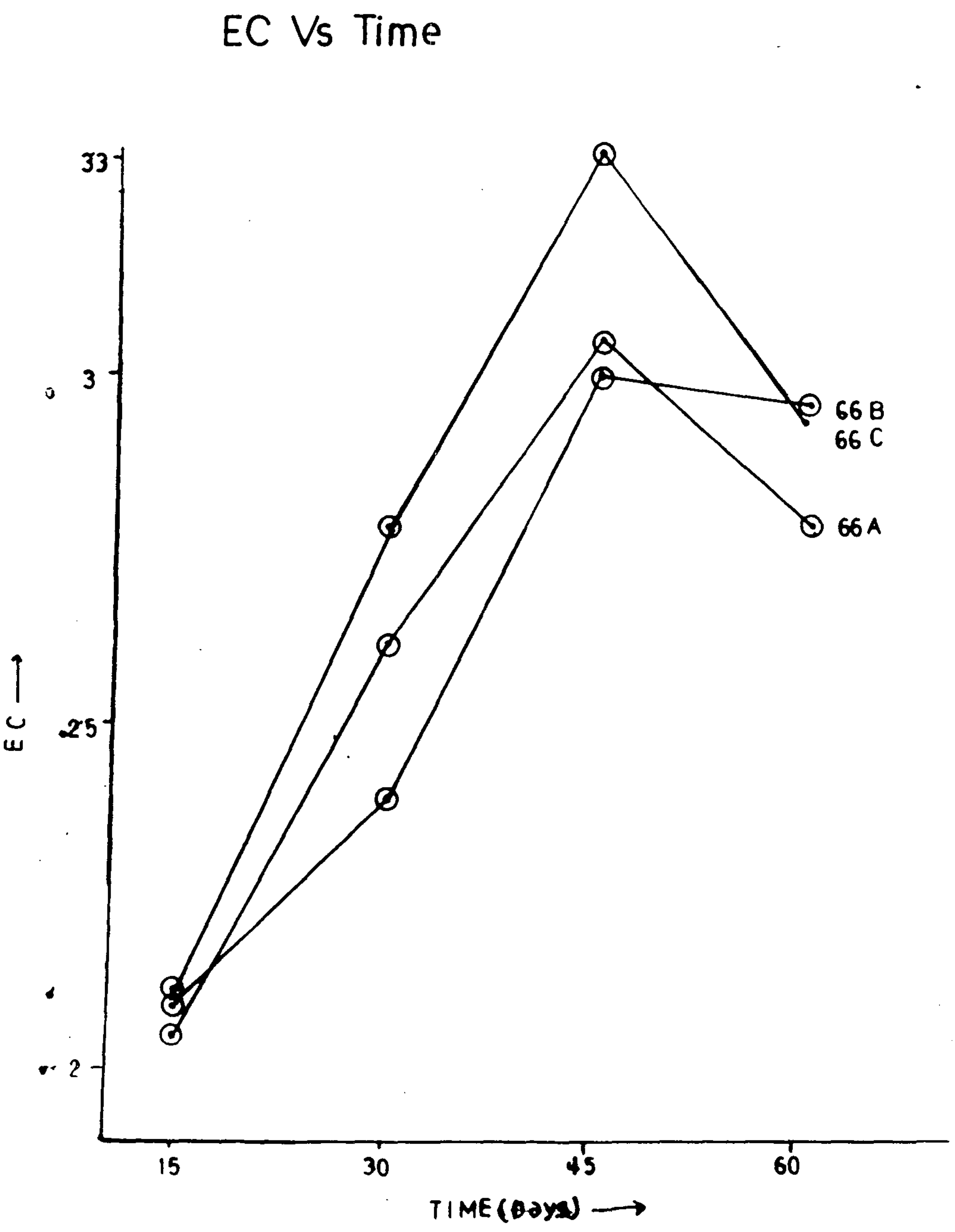


Fig. 3. Periodic changes in EC (m, mhos) of 66% S-T mixtures due to liming.

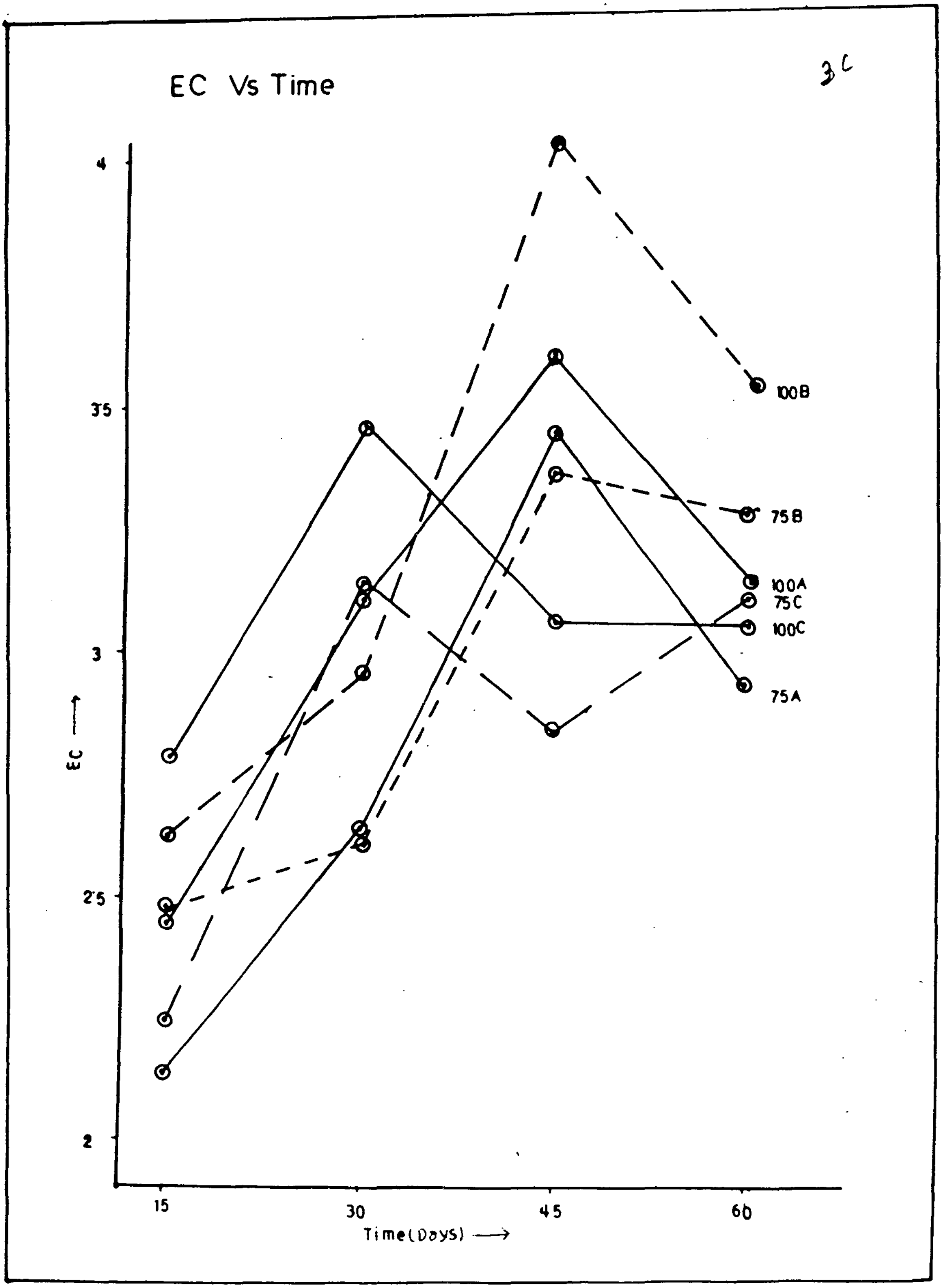


Fig. 4. Periodic changes in EC (m, mhos) of 75% S-T mixtures due to liming.

for all doses of lime except for 25C. But whthin a particlar mixture, the variations in EC with respect to three lime additions, were generally found to first decrease and then increase with the increasing amount of lime added, with few irregularities. With respect to tme, the EC values were increaseing till 45 days after liming and then decreaseing for all mixture and all lime additions except 100C.

From the graphical, representation (Fig. 2,3 & 4), it can be observed that uniformity in variations in EC over time trends to lessen as the percentage of tailings in mixture increased.

Electrical conductivity is related to the amount of soluble salts and the other ions present in the medium. So any factor, which may affect the number of ions and amount of soluble salts will be responsible for the variations in EC. EC was hightst for the 66% mixture followed by 100%, 75%, 50%, 25% and 33% before the application of lime. This means that in 66% soil-tailings mixture, any way the number of ions contributing to EC is highest and lowest in 33% mixture. The number of ions and soluble salts depends upon solublity products and ionic products of varous salts present in the system.

pH has a much marked influence on the solubility and hence on solubility product and ionic product.Tailings contain a numbr of heavy metal and number of anions, so a variety of salts will be there in tailings and the salts of these heavy metals will varry widely in their solubility with respect to pH. The variation of EC with respect to different lime additions, keeping the period constant, may be explained by the activity of K and Ca ions.

ORGANIC CARBON

Table-6 represents the periodic changes in organic carbon content of different soil-tailings mixture due to application of different amounts of lime. Tailings has much higher amount of organic carbon than soil itself, hence as we proceed from low to high tailings percentage mixture, organic carbon content decreases. High carbon content in tailings may be due to its impurity caused by the disposal of domestic refuse of the locality near the sites of sample collection and rapid variation in the nature of tailings may also contribute a little, in this respect (Kelly and Tuovinen, 1988).

Periodic values of organic carbon contents of table-6 indicates the loss of organic carbon for all soil-tailings mixtures, for all doses of lime. Loss of organic carbon was much in the case of mixtures, and tailings containing higher % of organic carbon initially. Among the three different lime additions, the highest loss was noted in the case of lime addition equal to double of the lime requirement for all soil-tailings mixtures and tailings itself. After sixty days of liming the organic carbon content was more or less found to be levelled of for all soil-tailing mixtures and tailiings and the value ranged from 0.19% to 0.3543%, where as before liming organic carbon content range was 0.264% to 0.83.

This decrease in organic carbon content may be attributed to the decompostion of organic matter following liming, which resulted in the loss of organic carbon as CO_2(Harmsen and van Scureven, 1957). Around netural and slightly alkaline pH range, the microbial activity is maximum and so it accelerates the decomposition of organic matter (Awad and Edwards, 1977) and hence the observed loss in organic carbon content of different soil-tailings mixtures and tailings.

AVAILABLE NITROGEN

Fig. 5 and 6 and table - 10, represent the periodic changes in available nitrogen content of different soil-

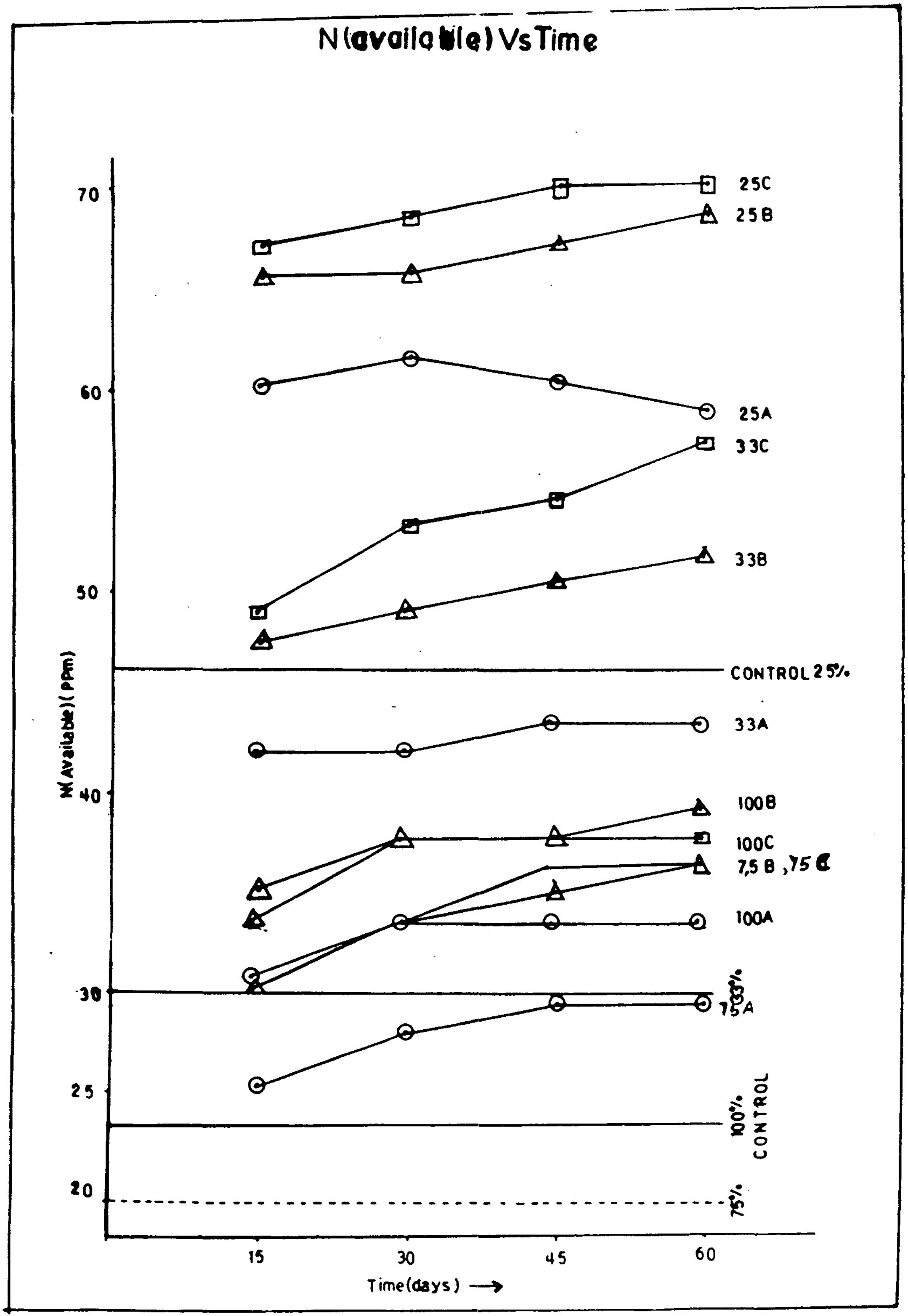


Fig. 5. Periodic changes Available nitrogen (ppm) of 25%, 33%, 75% S - T mixtures and tailings due to liming.

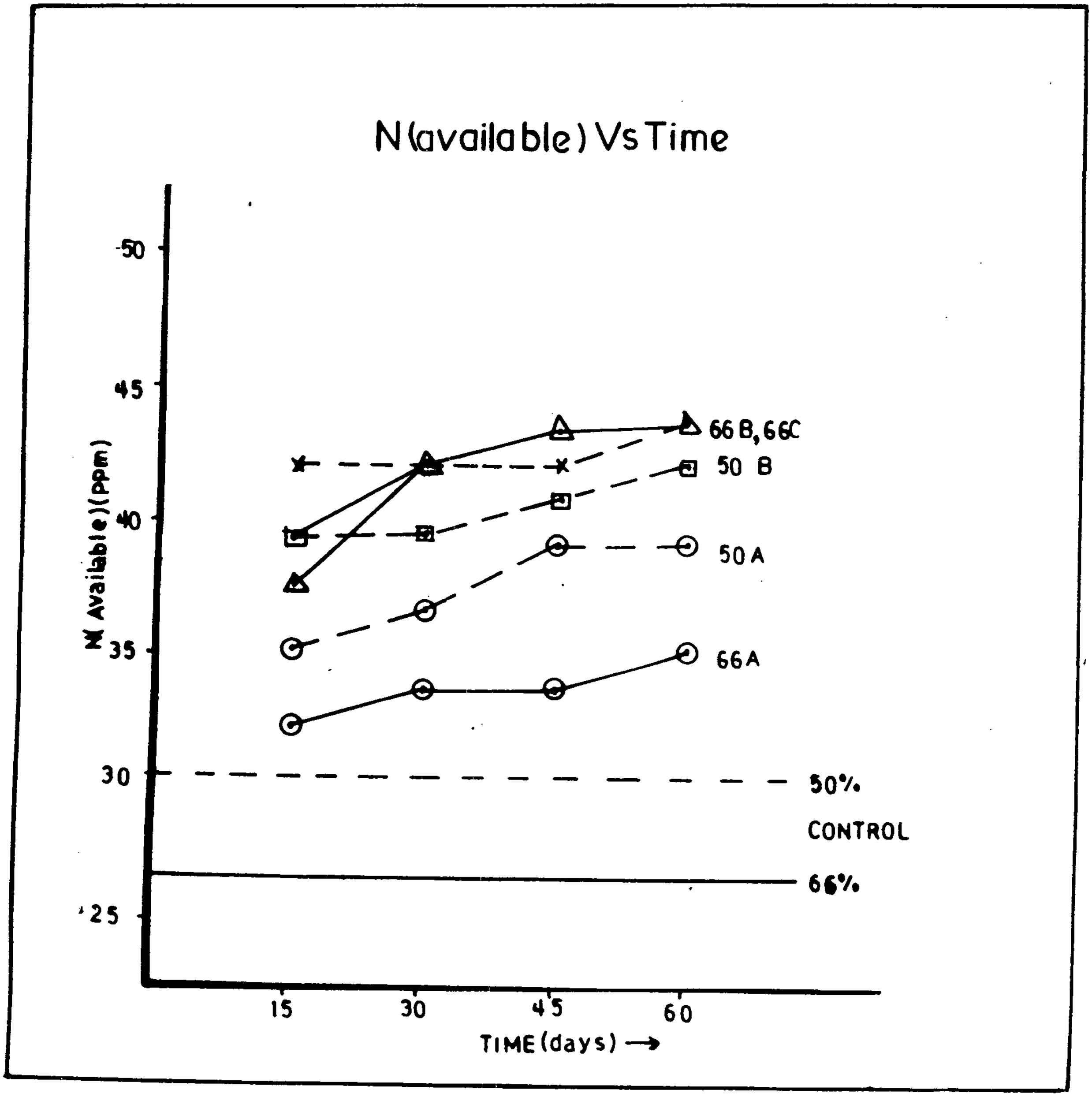


Fig. 6. Periodic changes Available nitrogen (ppm) of 50%, and 66% S - T mixtures due to liming.

tailings mixtures due to liming.Available nitrogen content of different soil-tailings mixtures at control level decreases with increasing amount of tailings except in pure tailings. As far as literature is concerned, it points out that tailings are generally devoid of availabilty indexes of major plant nutrients. So this much value of available nitrogen, may be due some impurity in tailings. Another point in this connection is to be mentioned that the tailings pond site was also the site for disposal of domestic refuges of the locality. The tailings dams and waste-deposits represent extermely complex and variable environment. variations in the nature of tailings occur between different section of the same dam as a result of change in the grade of run-of-mine feed, fluctuation in mettallurgical extraction efficiency and in the physical characteristics of the dam including water availablity and depth.

It is evident from the table - 6 that lime additions increase the availablity of nitrogen proportionately for all doses of lime and for all soil-tailings mixtures. This may be explained on the basis of the fact that mineralization of soil nitrogen increases with increase in pH and liming has stimulatory effect on the microbial activity leading to the mineralization of soil nitrogen.

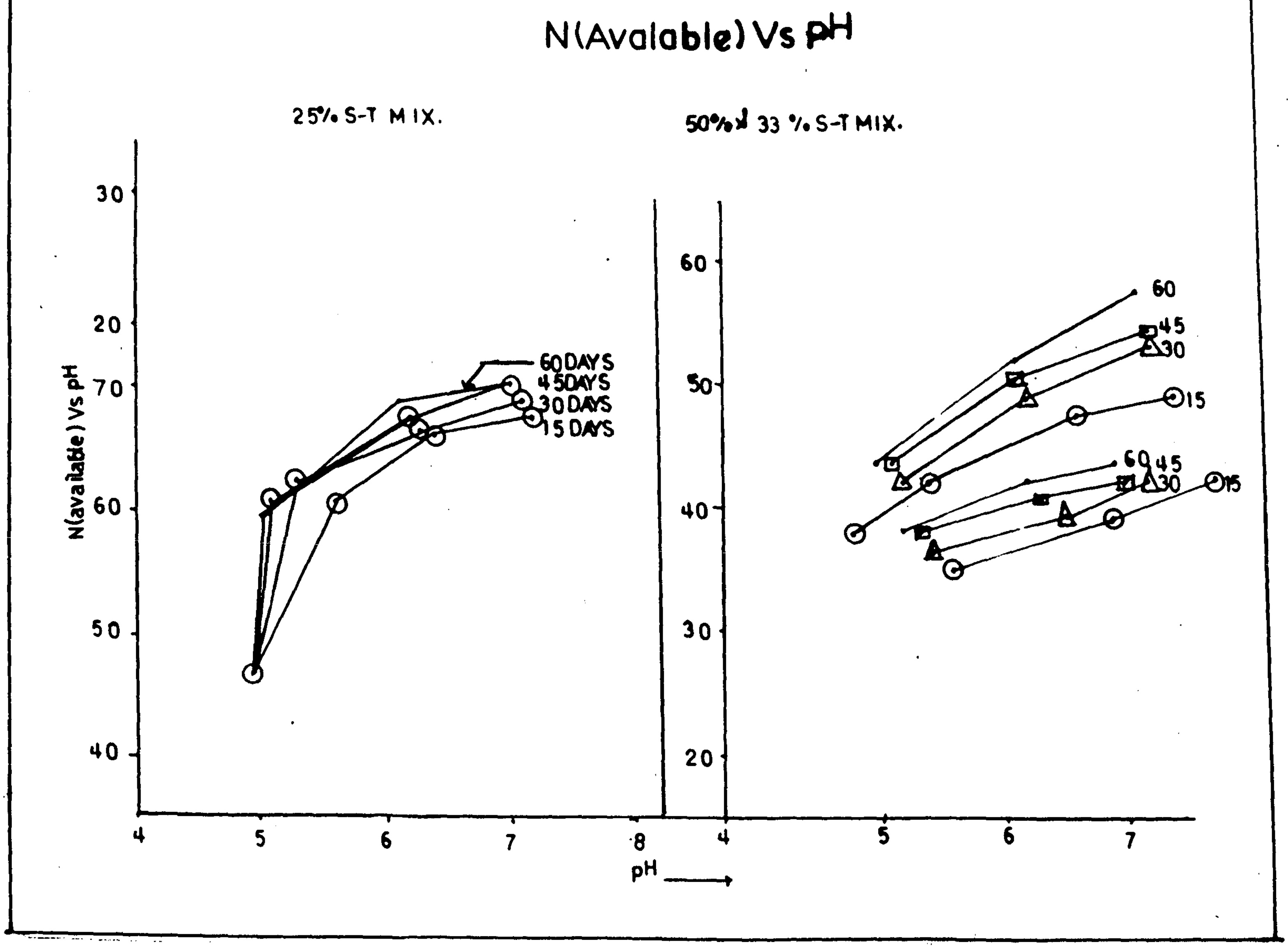


Fig. 7. Effect of liming (pH) on N-Availability of 25%, 33% and 50% S-T mixtures over a period of 60 days.

With respect to time the available nitrogen content increases after lime application for all the time except in one or two cases. This increase in available nitrogen content with respect to time is not infulenced by the little variation in pH. This increase in mineralization over time may be due to the fact that effect of liming in stimulating mineralization is maintained over long time (Allission and Sterling, 1949). Another factor which may be taken into account to explain the increasing mineralization of soil nitrogen inspite of a general decreasing trend in pH is temperature. The mean daily temperature during the concerned study period varied from 16^{o}C to 33^{o}C and we know that increasing temperature activates microbiological activity, hence mineralization of soil nitrogen within a certain temperature range.

From Fig. 5,6, & 7, it can be concluded that available nitrogen content of various soil-tailings mixture with all three lime additions was more or less uniform till 45 days with few variation. Few variations are always there in every trends and like pH and EC, we also find more variable results from the mixtures with higher tailings percentage than the mixtures with higher soil percentage. This is always due to complex and variable nature of tailings.

Availablity of nitrogen is a fuctions of number of factors such as soil pH, soil miosture, temperature, rate of liming, organic matter, total nitrogen content etc. All these factors operate simultaneously in the soil eco-system and it is very difficult to single out the contribution of each.

AVAILABLE PHOSPHOROUS

Periodic variations of phosphate availability of different soil-tailings mixture following liming are being shown in table - 11 and Fig. 8 & 9. For all soil-tailings mixtures, liming increased the phosphorous availablity, for all doses of lime additions. This increasing trend in phosphorous availability was maintained till 30 days with few variations. However, the available phosphorous for all soil-tailings mixtures after 60 days was more than control level for respective soil-tailings mixture and respective lime additions.

25% and 33% soil-tailings mixtures showed decreasing trend over time, but final values of available phosphorous were higher than control value. 50% and 66% soil-tailings mixture followed almost decreasing pattern for 'A' and 'C' lime additions, but for 'B' lime addition, phosphorous availability went maximum after 30 days and then decreased.

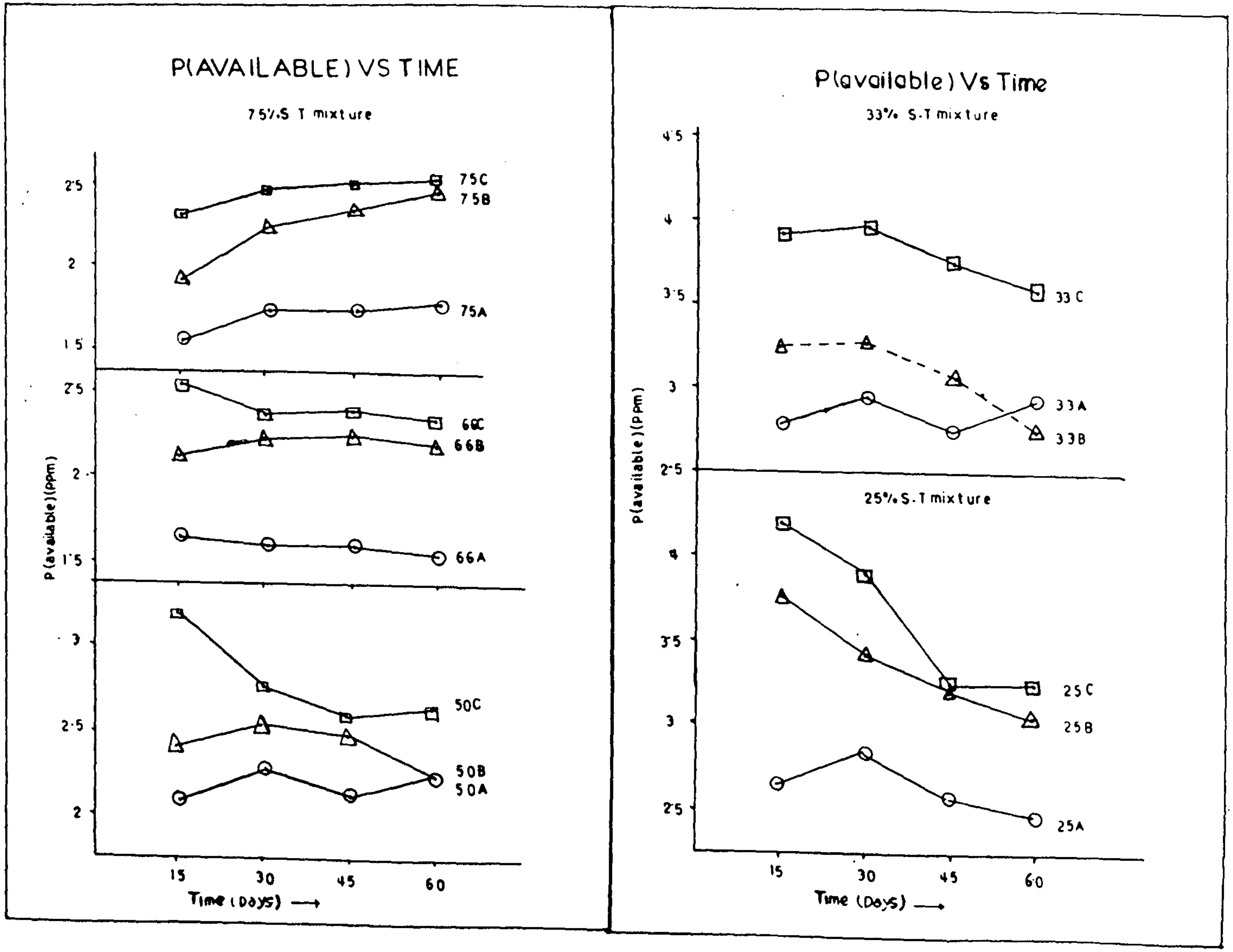


Fig. 8. Periodic changes in P-Available (ppm) of different S-T mixtures due to liming.

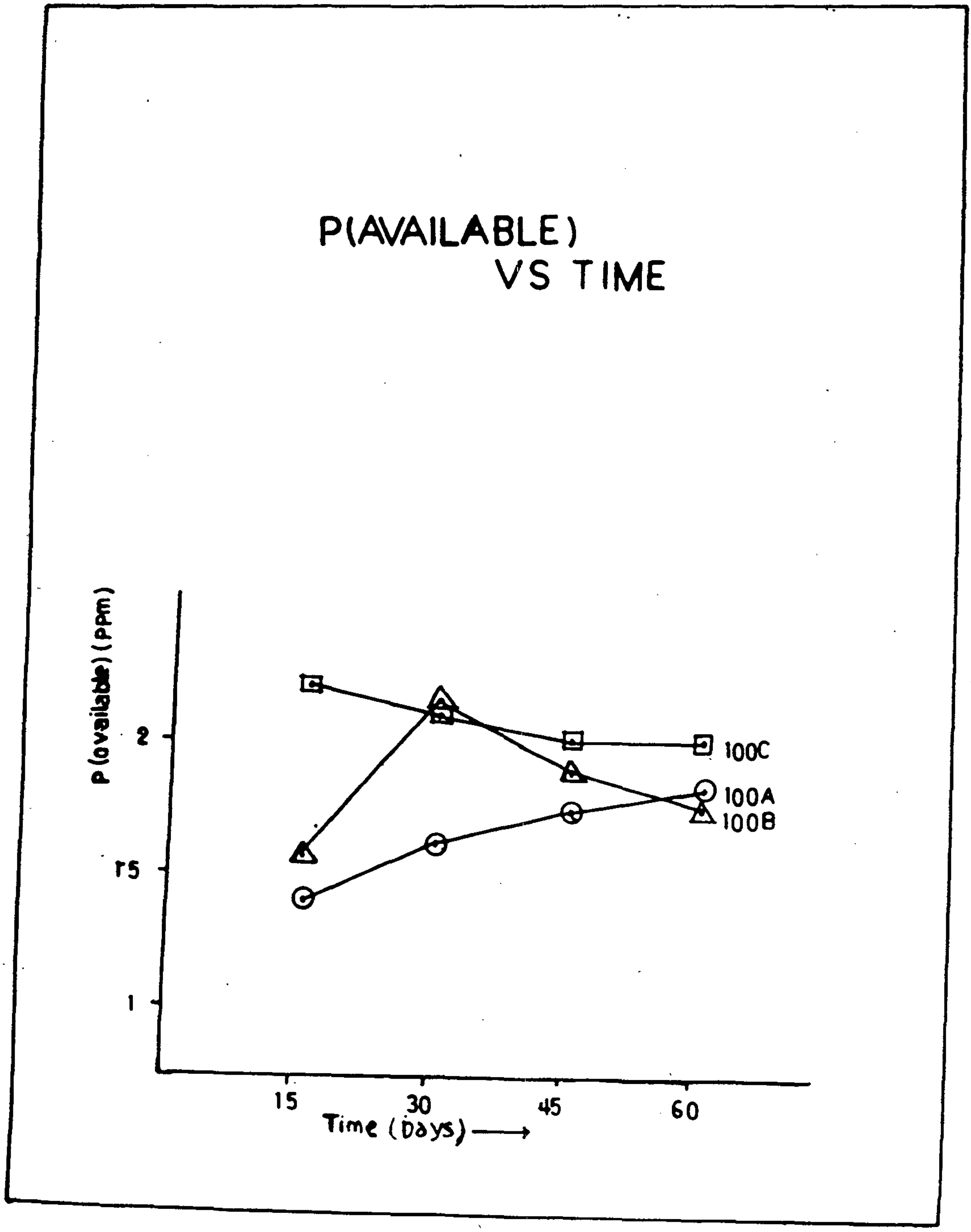


Fig. 9. Periodic changes in P-Available (ppm) tailings due to liming.

'A' lime addition increased phosphorous availability all time for 75% soil-tailings mixture and tailings only, whereas for B and C lime additions the availability increased till 45 days in 75% and till 30 days in tailings, followed by decrease.

From Fig. 8 & 9, it appeared that for 'A' lime additions, phosphorous availability proceeds no uniform increasing or decreasing trends in soil-tailings mixture high in soil percentage to increasing trends in mixtures higher in tailings percentage with respect to time, through almost linear curve for 66% mixture.

For the treatment 'B' we get a decreasing trends for high soil percentage mixture, increasing pattern for 75% mixture and a linear curve for 66% mixture, with respect to time. The similar kind of phenomena also was observed in the case of the treatment 'C' with the exception of tailings.

From Fig. 10 to 14, we find that phosphorous availability increases with pH and high doses of liming resulted in high phosphorous availablity with few variations.

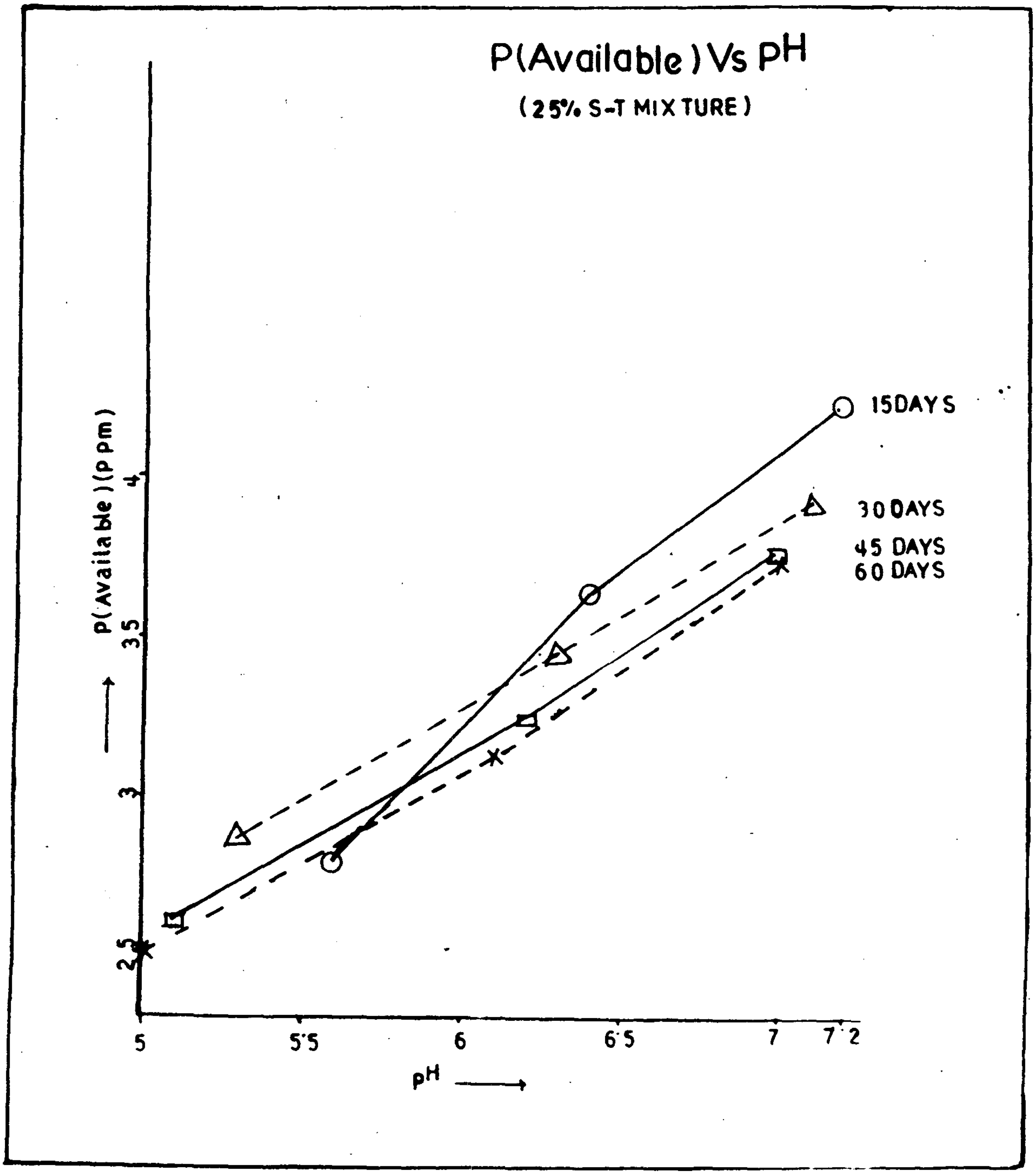


Fig.10. Effect of liming (pH) on P-Availability of 25%, S-T mixture over a period of 60 days.

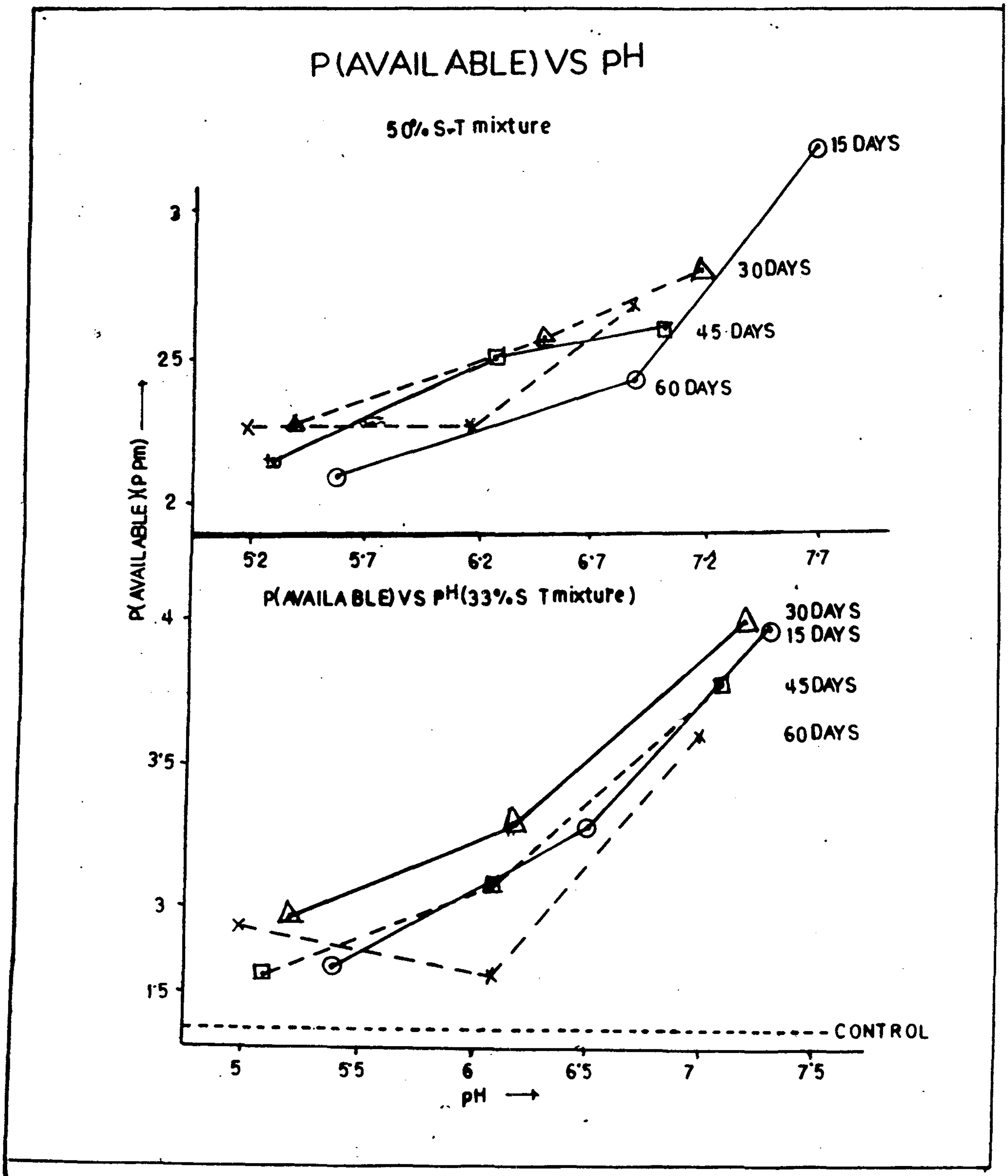
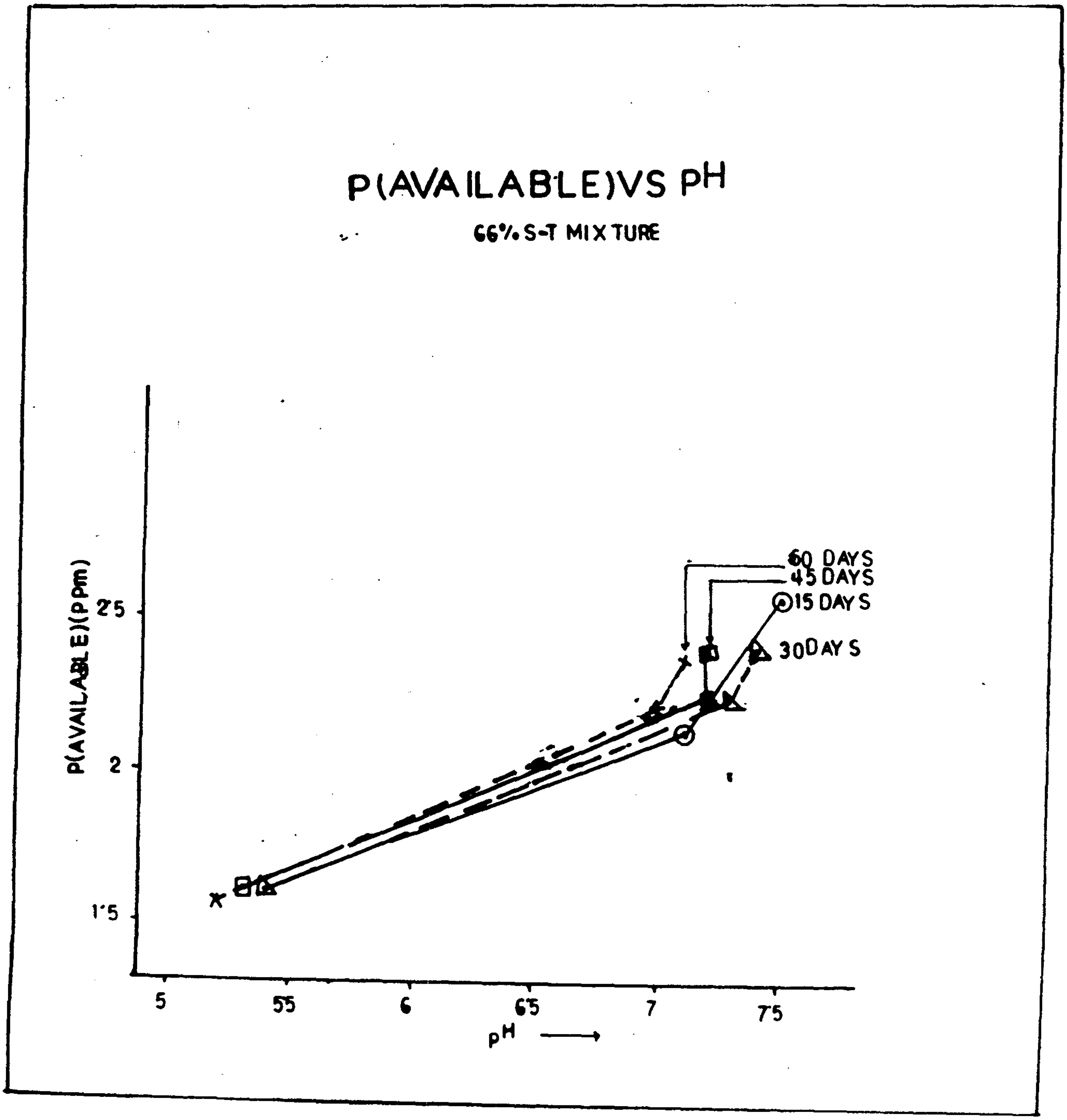


Fig.11. Effect of liming (pH) on P-Availability of 33% and 50% S-T mixtures over a period of 60 days.



ig.12. Effect of liming (pH) on P-Availability of 66% S-T mixture over a period of 60 days.

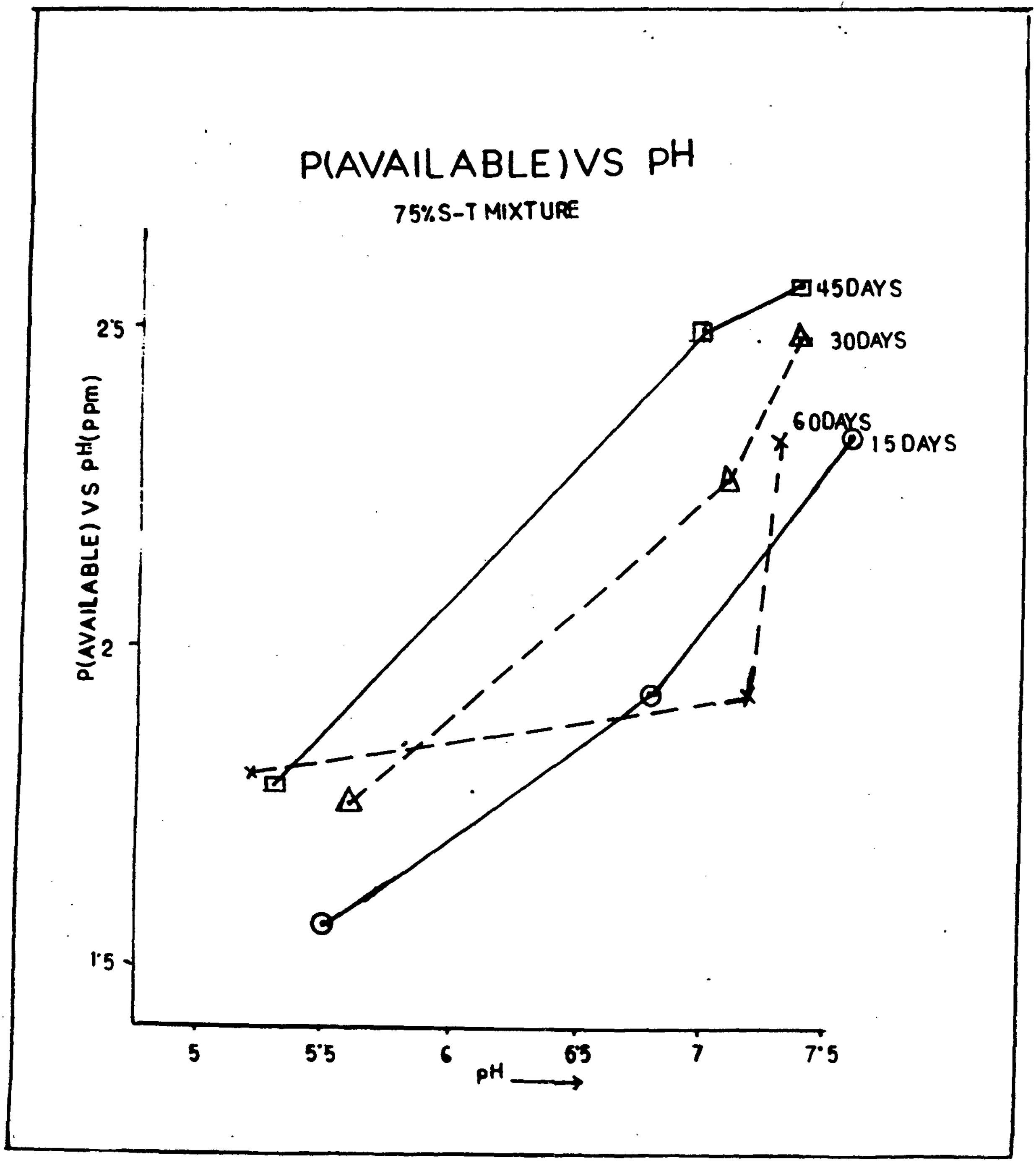


Fig.13. Effect of liming (pH) on P-Availability of 75% S-T mixture over a period of 60 days.

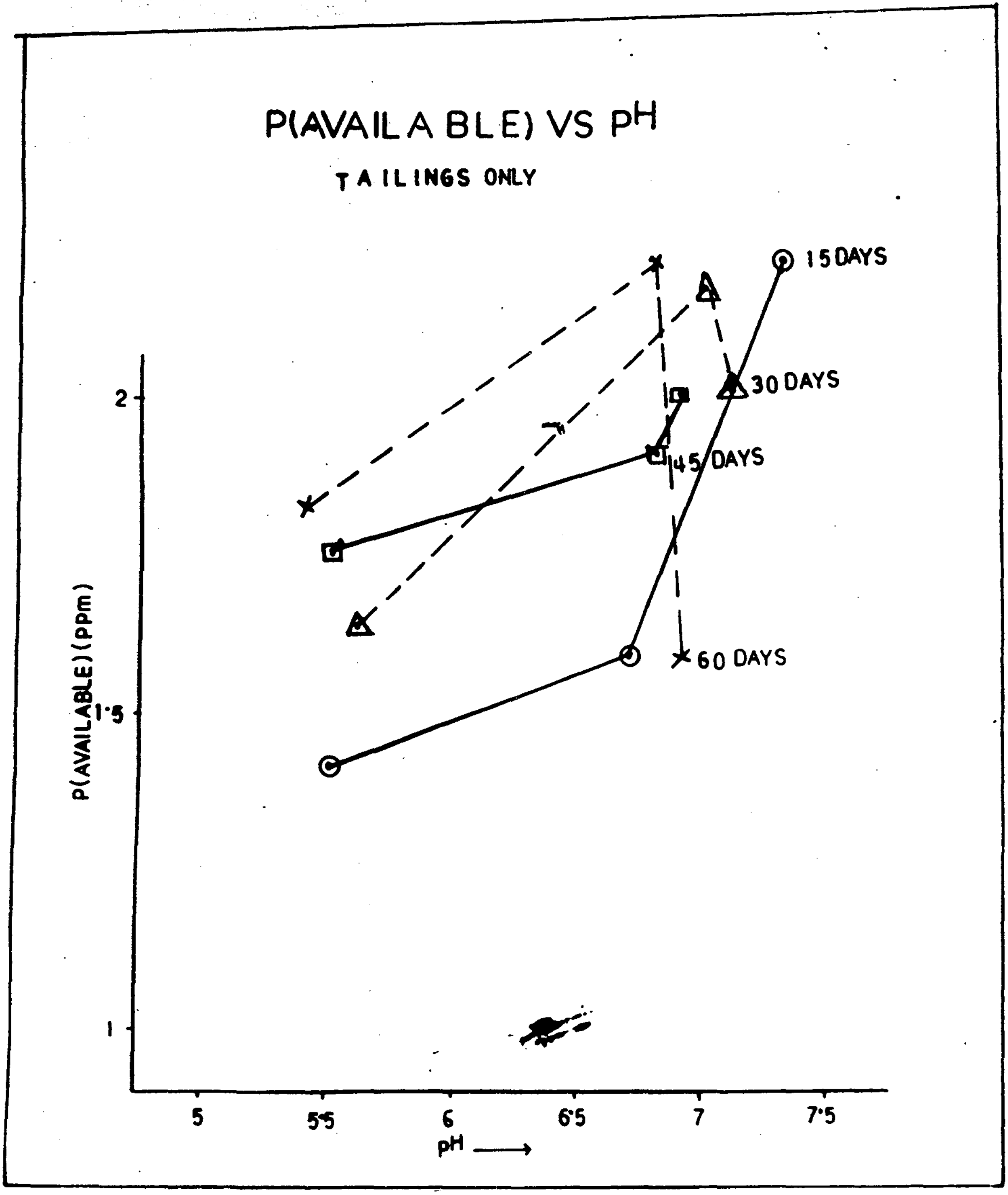


Fig.14. Effect of liming (pH) on P-Availability of tailings over a period of 60 days.

These variations are due to complex physical , chemical and microbiological interactions between lime applied soil and tailings within the stipulated time frame work. Soil, itself is a complex system and variation in one characteristics is affeected by numbers of other parameters simultaneously, so it is very difficult to explain these variations.

Increase in phosphorous availability following liming is due to increase in pH of the all soil-tailings mixtures. This may be due to adsorption of phosphate on hydrated Al and Fe oxides and precipitation of various Fe and Al phosphate compounds at low pH. Liming which increases the pH reduces the concentration of soluble and exchangeable Fe and Al ions, which otherwise forms sparingly soluble Fe and Al phosphates. Increase in pH may also results in hydrohysis of various Fe and Al phosphate to release the PO_4 ions in soil solution (Sample et.al., 1980). Maximum phosphate adsorption takes place in the pH range 2 to 4 (Obihara and Russel, 1972) and phosphate adsorption by both hydrated Al and Fe surfaces decreases till pH 7.

Periodic variations of soil-tailiings mixtures high in soil percentage, where phosphorous availability decreased overtime, may be accounted for the variation in pH. The

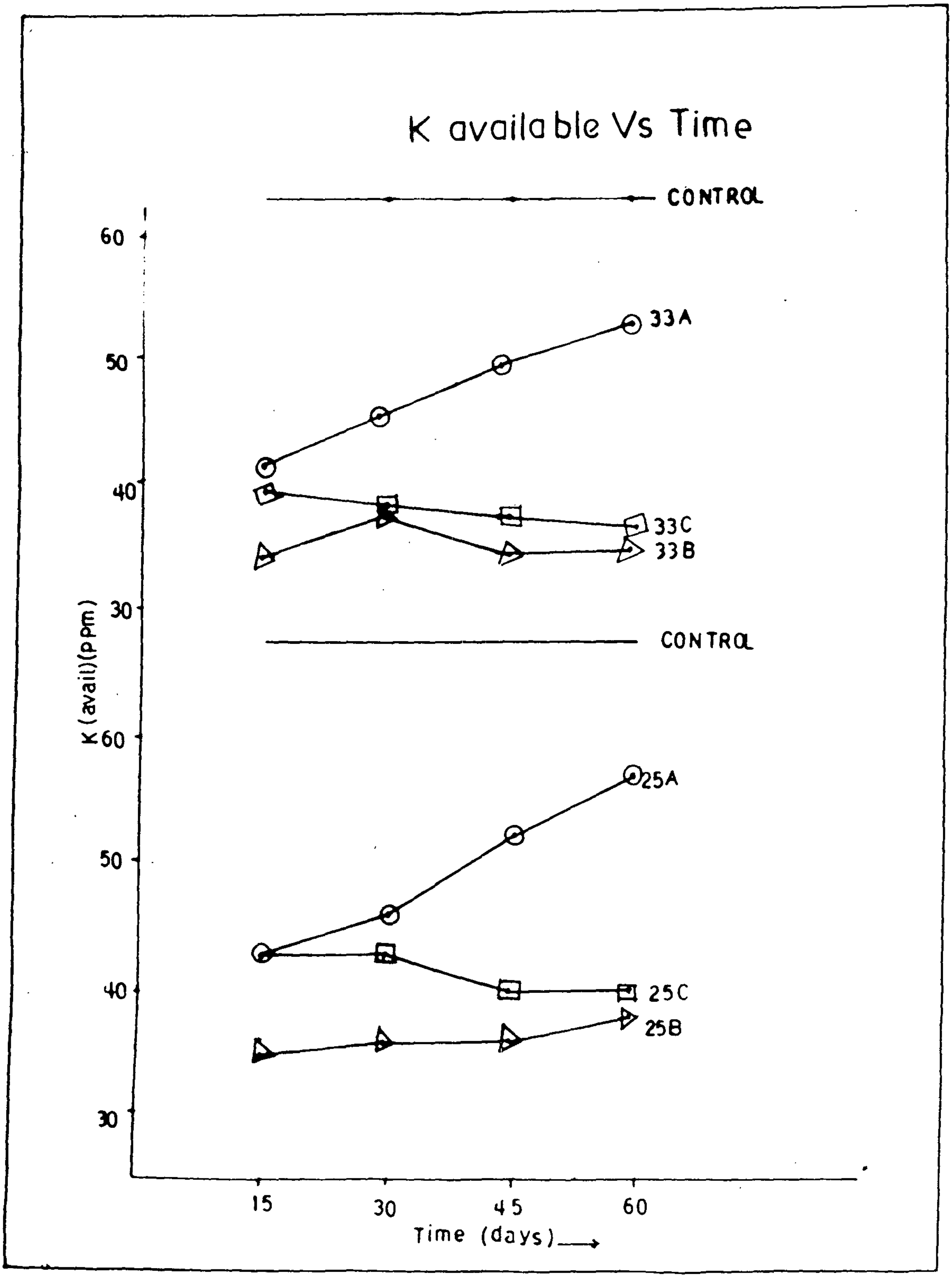
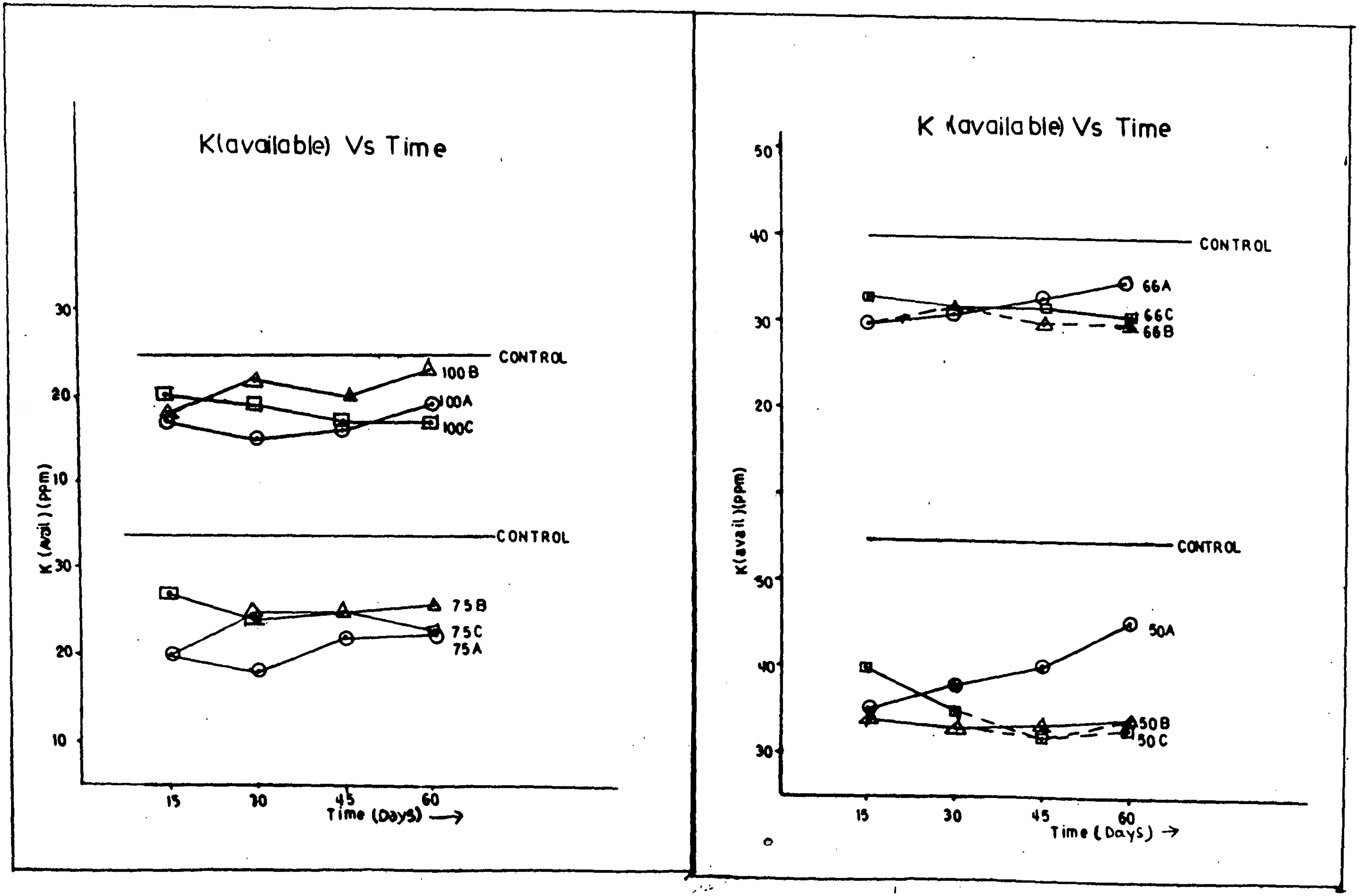


Fig.15. Periodic changes in K-Available (ppm) 25% and 30% S-T mixtures due to liming.



Periodic changes in K-Available (ppm) 50A decrease in pH decreases the phosphorous availability. On the contrary mixtures high in tailings percentage can be said to follow more or less increasing trends inspite of decreasing pH. This may be due to the release of some phosphate from tailings form unavailable to available form.

AVAILABLE PATASSIUM

Variation in potassium availability in different soil-tailings mixtures with different addition of lime is shown in table - 12 and Fig. 15 & 16. The availability of potassium decreased for all soil-tailings mixture for all lime additions and after 60 days following liming available potassium level was lower than the control value. Periodic values of available potassium reveal that there is a periodic increase in potassium availability for all soil-tailings mixtures with the lime addition equal to the half of the lime requirement (A) and a decreasing pattern of potassium availability was observed in rest two lime additions. There was an increase in potassium availability for (B&C). The treatment 'A' was much marked than other trends. Decreasing pattern was good for the mixtures high in soil percentage, but was not so in the mixtures high in tailings percentage and trends detoriated as percentage of tailings increased in the mixtures. High tailings percentage also affected the increasing trends for first lime addition

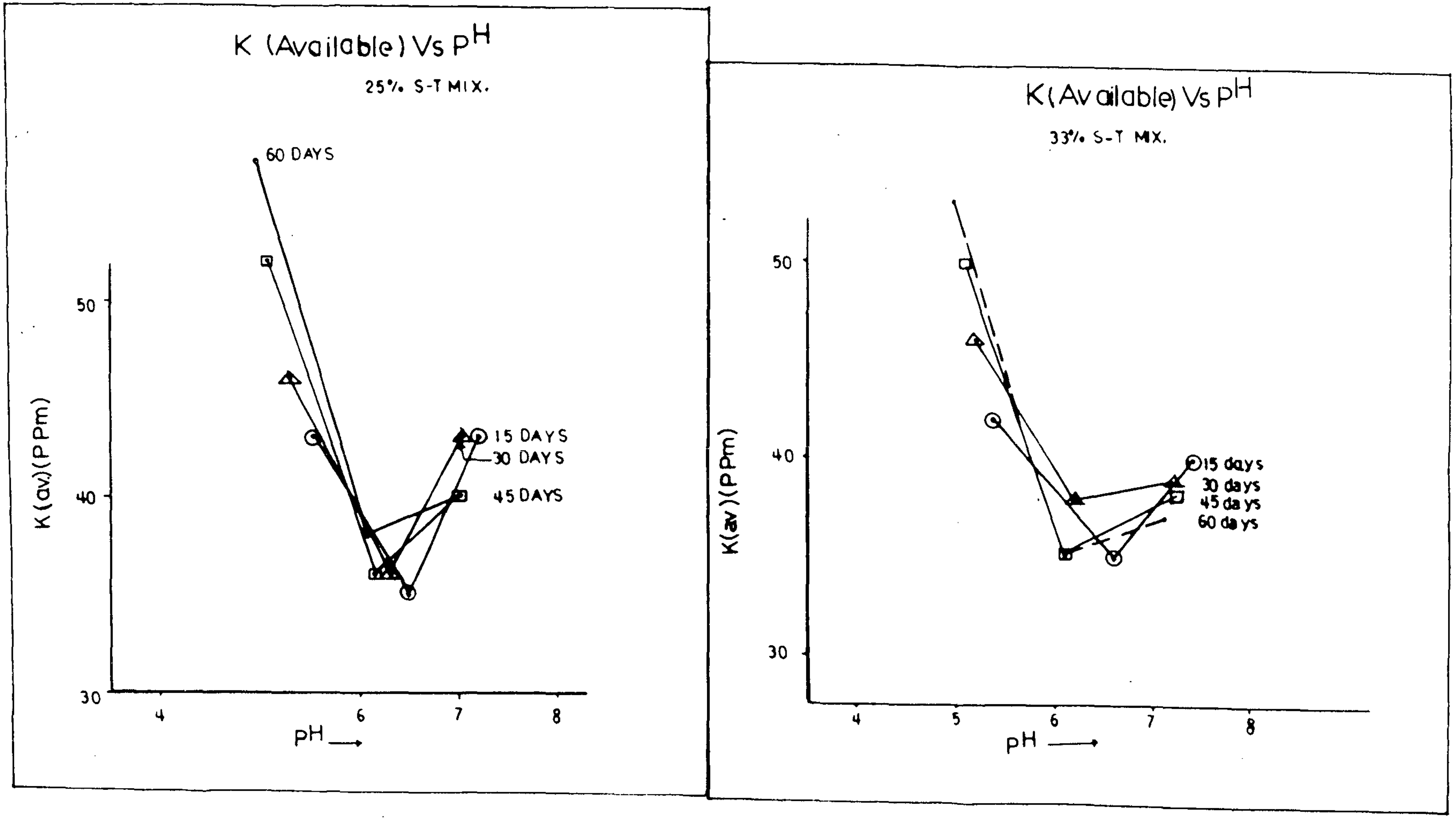


Fig.17. Effect of liming (pH) on K-Availability 25% and 33% S-T mixtures over a period of 60 days.

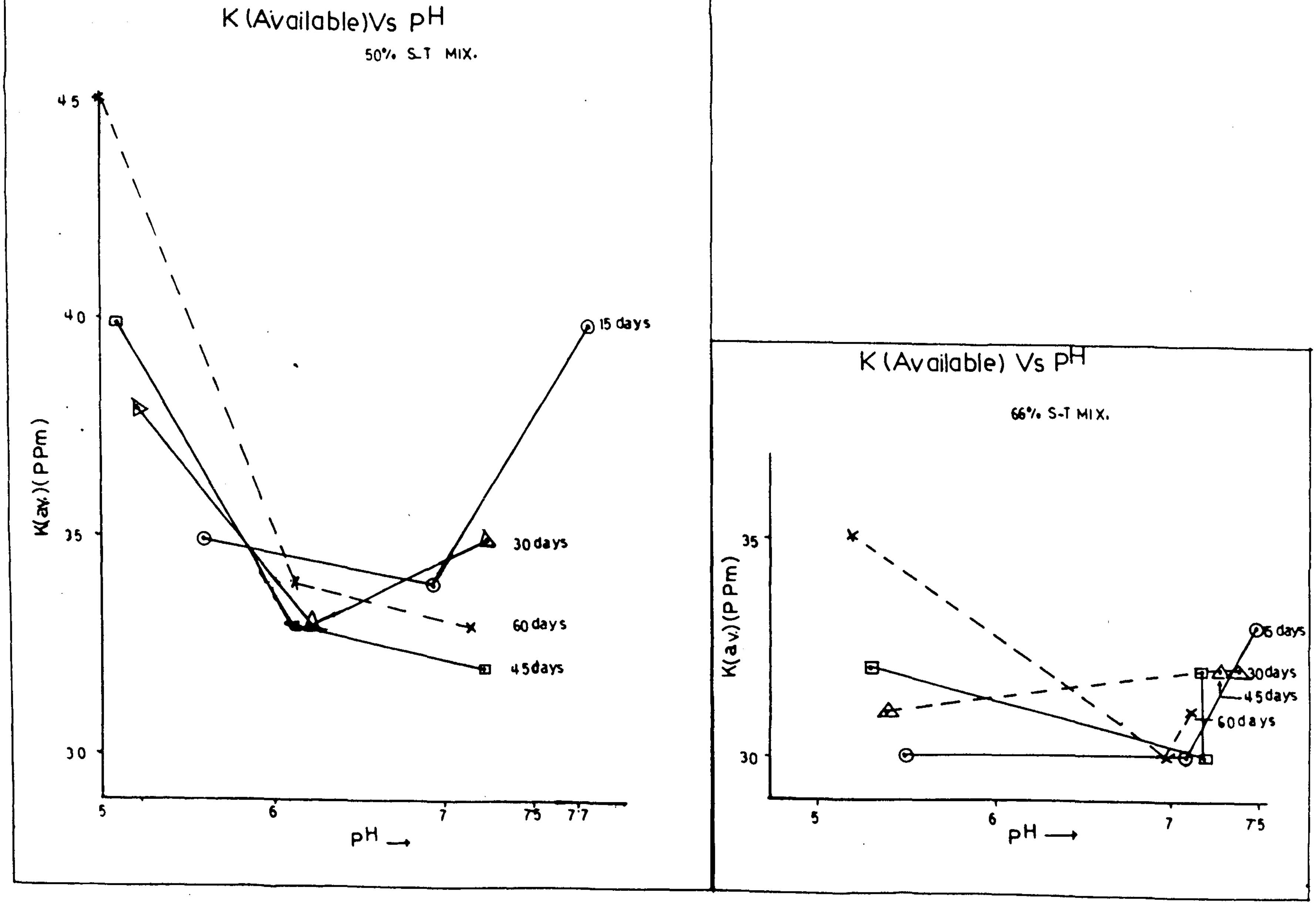


Fig.18. Effect of liming (pH) on K-Availability 50% and 66% S-T mixtures over a period of 60 days.

also.

The effect of pH on potassium availability can be observed from Fig. 17 & 18. It indicated that with respect to pH available potassium tends to decrease first with increasing pH till 6.0 to 6.7 and then increases further with increase in pH with few exceptions. All periodic variations of different mixture can be correlated with pH variations.

The decrease in availablity of potassium with soil pH and so with liming may be due to the opening up of K-selective exchange site that were blocked by Al at lower pH (Nemeth and Grimme, 1972) or it may be due to the lowered percent K saturation caused by increased CEC (Bratlett and McIntosh, 1969). The trends of decreasing solution K following liming may be as a result from the increased "pull" on the solution K by new CEC as the CEC increases, the selectivity for Ca increase at the expense of K (Pratt et. al., 1962)

Increase or decrease in potassium availability periodically for different lime additions is due to the corresponding value of pH. This indicates that liming effect on potassium availability does not maintain for a long time and even a slight change in pH , changes the solution K and hence its availability.

TOTAL NITROGEN,TOTAL PHOSPHOROUS & TOTAL POTASSIUM

Total nitrogen content of all soil-tailings mixture with all lime addition decreased following liming and decrease was maintained over time as shown in table 7,8&9.

The decrease in total nitrogen content was more in the case, where soil-tailings mixtures having more total nitrogen content before liming. In all these cases the total nitrogen content were found to decrease more for the lime addition equivalent to double of the lime requirement.

The decrease in total nitrogen content may be due to the loss of nitrogen through various processes i.e. denitrification and ammonia voltalization and in the form of N_2 and NH_3gas. Around pH 7.0 the microbial activity is seepposed to be at their maximum,so both denitrification and nitrification proceed rapidly (Harsmen and vanschrven,) Nitrogen content of soil and soil like materials is also known to decrease with rise in temperature. And, during the concerned study period the mean daily temperature increased from 16^{o}C to 33^{o}C .Another point in this connection here is to made is that liming accelerates the decomposition of

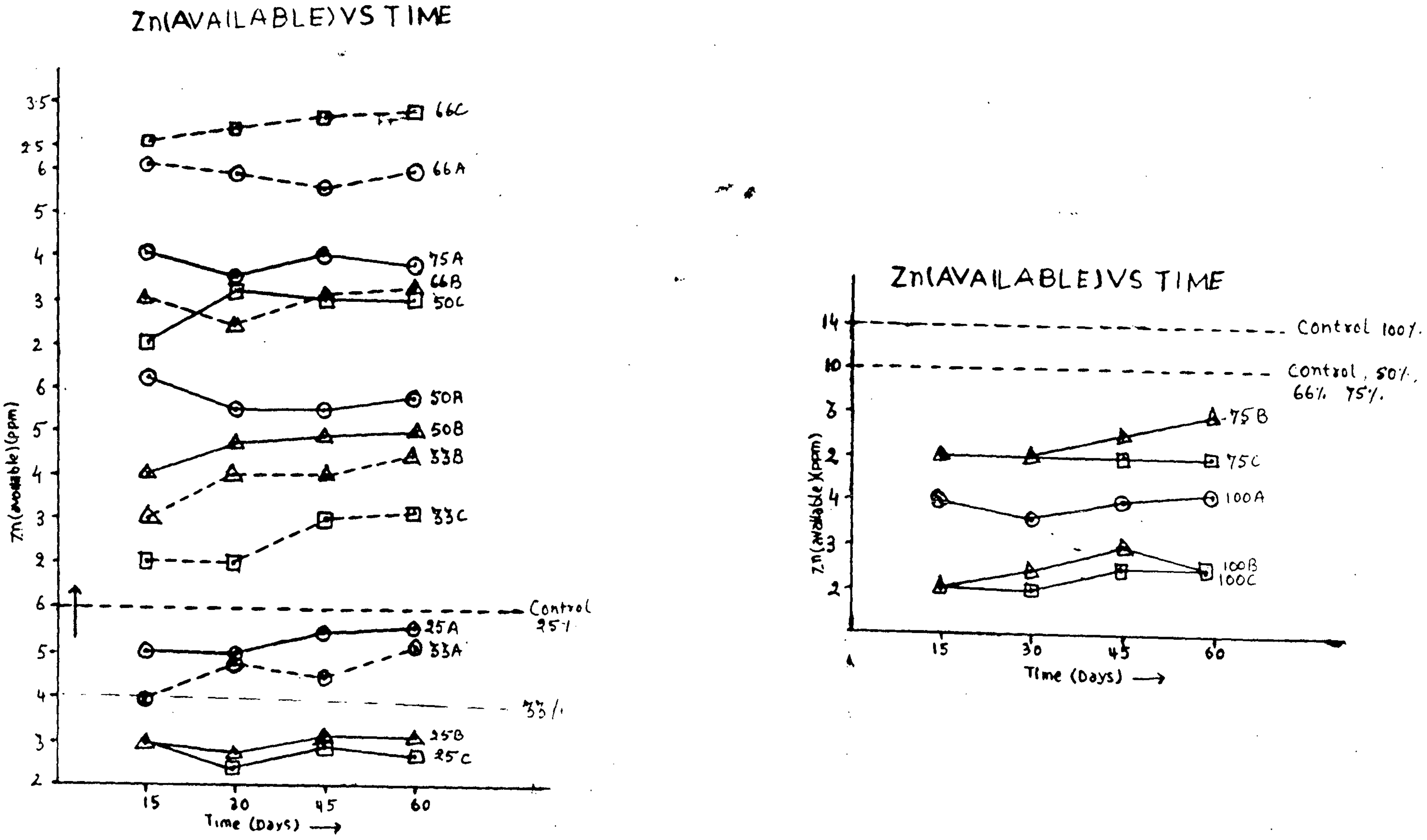


Fig.19. Periodic changes in Zn-Available (ppm) of different S-T mixtures and tailings due to liming.

organic matter. Marn et. al.(1972) found that energy required for the denitrification energy is provided by sulfur contained in tailing. The loss of nitrogen from the mixtures with lime addition equivalent to double of the lime requirement may be due to increase in mineralization process at corresponding high pH and so more possibility of loss of nitrogen to atmosphere.

Content of all soil-tailings mixtures are recorded in table - 7,8 & 9. From thus tables it would evident that total phosphorous and during theentire period of this experiment remained more or less constant, thereby showing that liming had very little effect on the overall budget of total phosphorous and total potassium of these soil-tailings mixtures and tailings itself.

AVAILABLE ZINC

Avilablity of Zinc in different soil-tailiings mixtures and their periodic variations with different lime addition has been shown in table - 14 and Fig. 19. Availability of Zn incerased as the percentage of tailings increased, but it remained constant at 10ppm level for apprieliable range. Liming of all soil-tailings mixture reduced the concentration of solution Zinc for all soil tailings

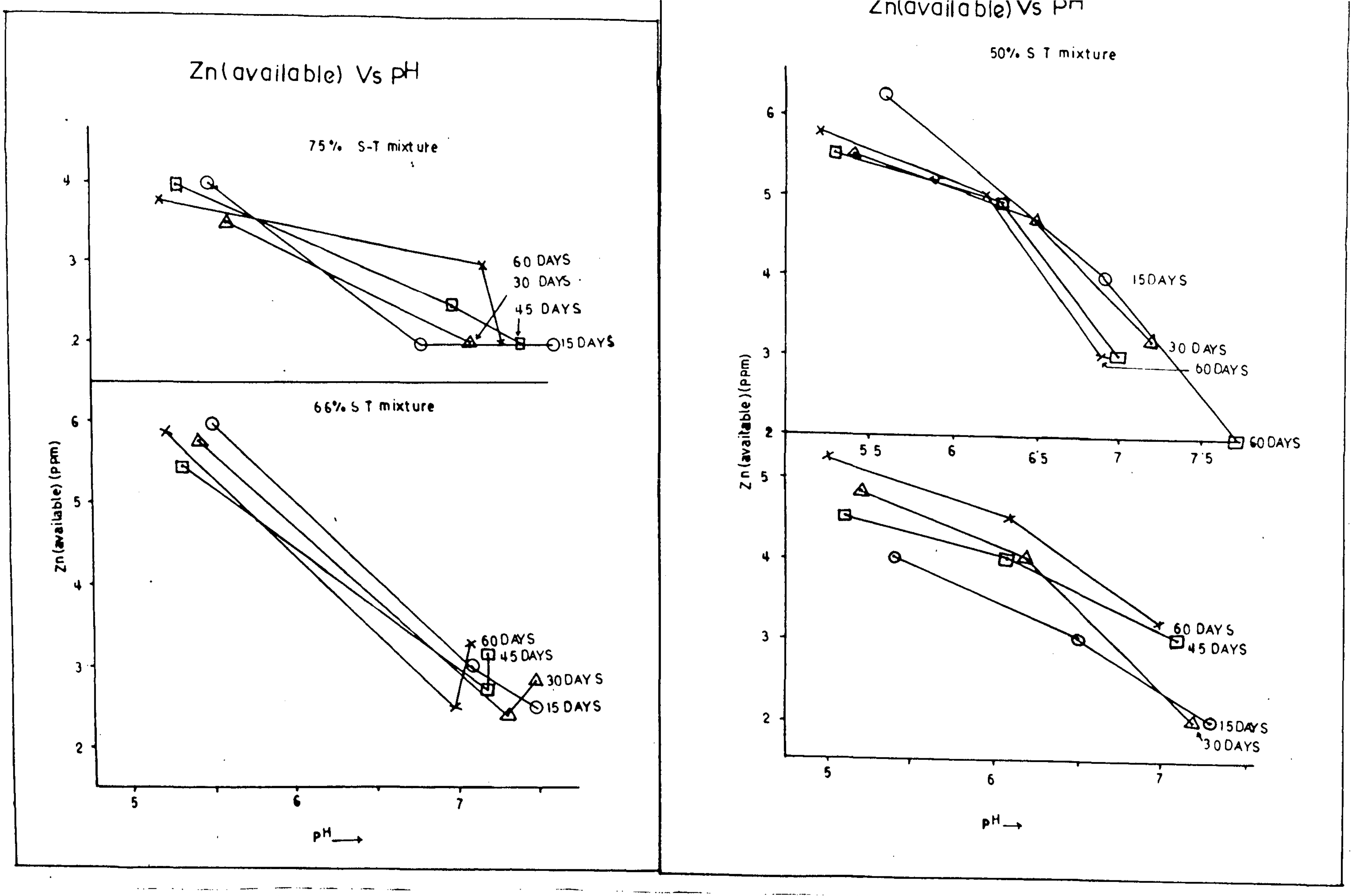


Fig.20. Effect of liming (pH) on Zn-Availability 33%, 50% and 66% 75% S-T mixtures over a period of 60 days

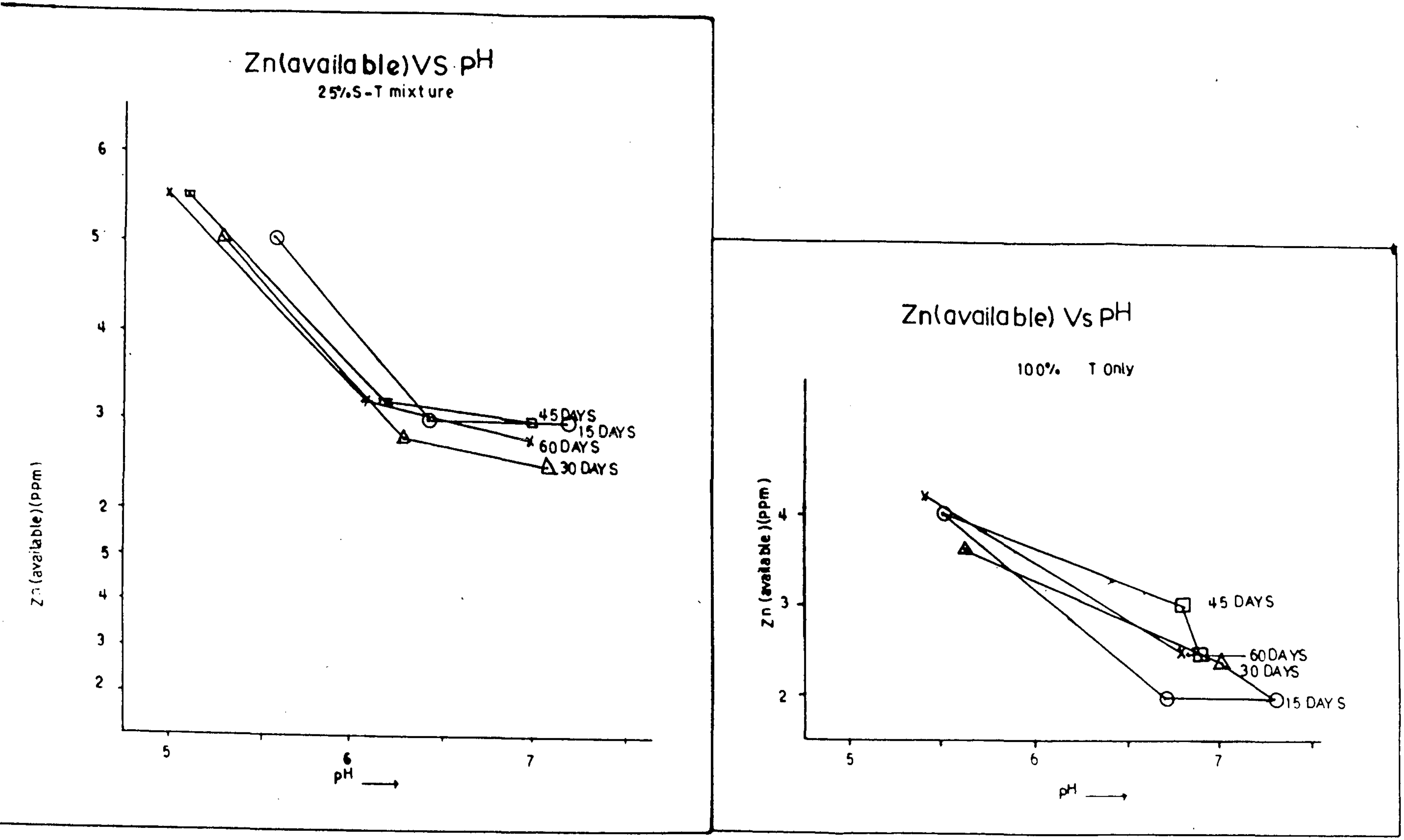


Fig.21. Effect of liming (pH) on Zn-Availability 25% S-T mixture and tailing over a period of 60 days.

mixtures andn reduction in available Zinc has very much effective in the high tailings perecntage mixture. Periodic variations although showed mixed trends in Zinc availability, but for all soil-tailings mixtures and tailings itself value for all doses of lime additions and for all soil-tailings mixtures. Periodic incerase or decrease in Zinc avialability however, were not much and ranged from 0.1 to 1.5 units.

Decrease in availablity of Zinc with pH can be observed from the Fig. 20 & 21, and we find that the zinc availability decreases with pH with respect to time after liming. So we can say that effect of liming on zinc availability in maintained over time.

Decrease in zinc solubility with increasing pH may be accounted for by generation of pH dependent charge sites on organics or clays, (Bache, 1976). Like copper,zinc also bound to silicate clays. So zinc adsorption on Fe and Al hydroxide surfaces may be responsible for decrease in zinc solubility with increasing pH in soil and soil like systems. (Kinniberg et. al. , 1976) and we know that only a traction of adsorbed Zn^{2+} being in the exchangeable form (Kalbasi et. al., 1978). Another factor, which also might be playing its role in the solubility of zinc in soil solution

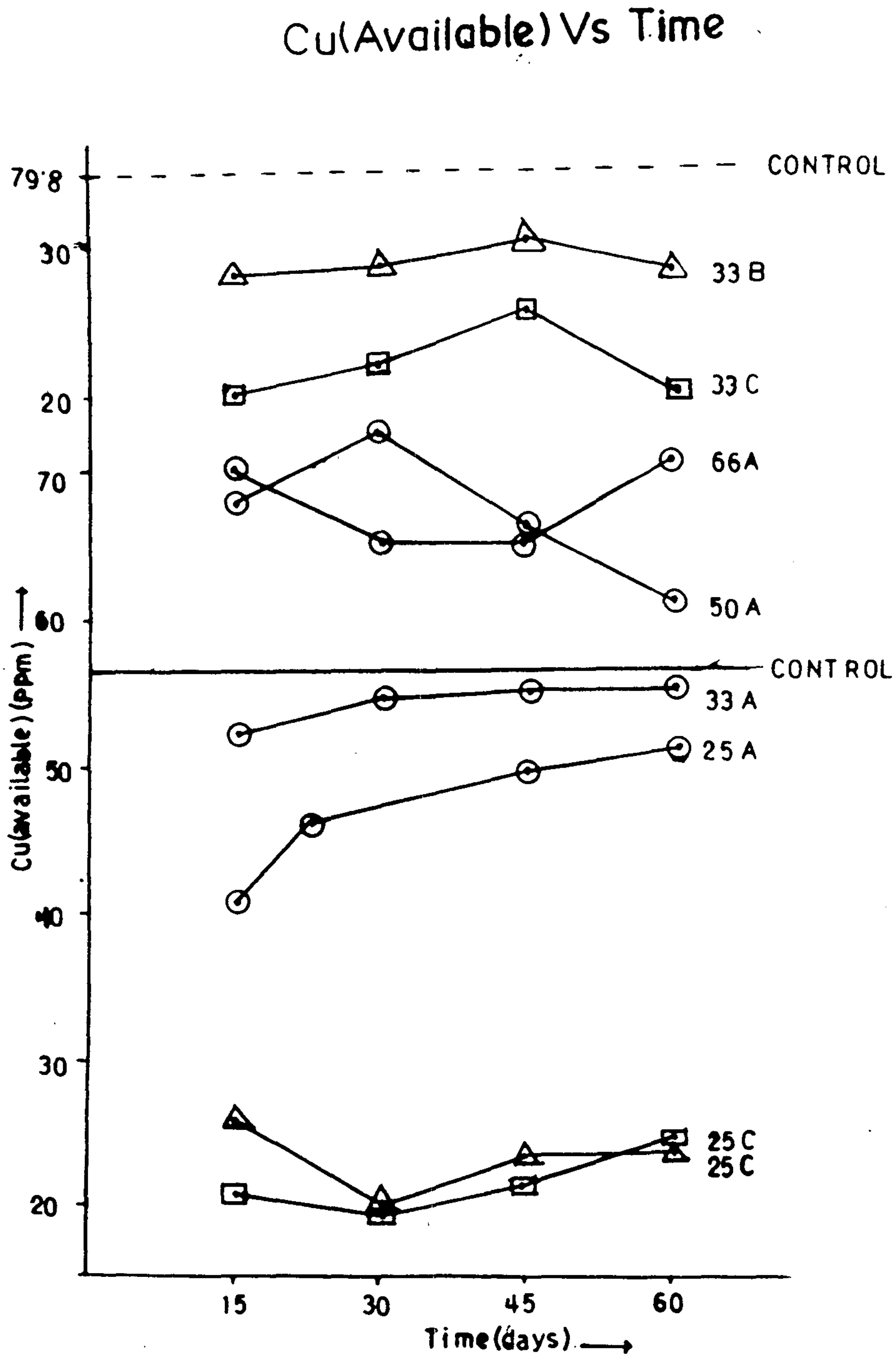


Fig.22. Periodic changes in Cu-Available (ppm) of 25% and 33% S-T mixtures due to liming.

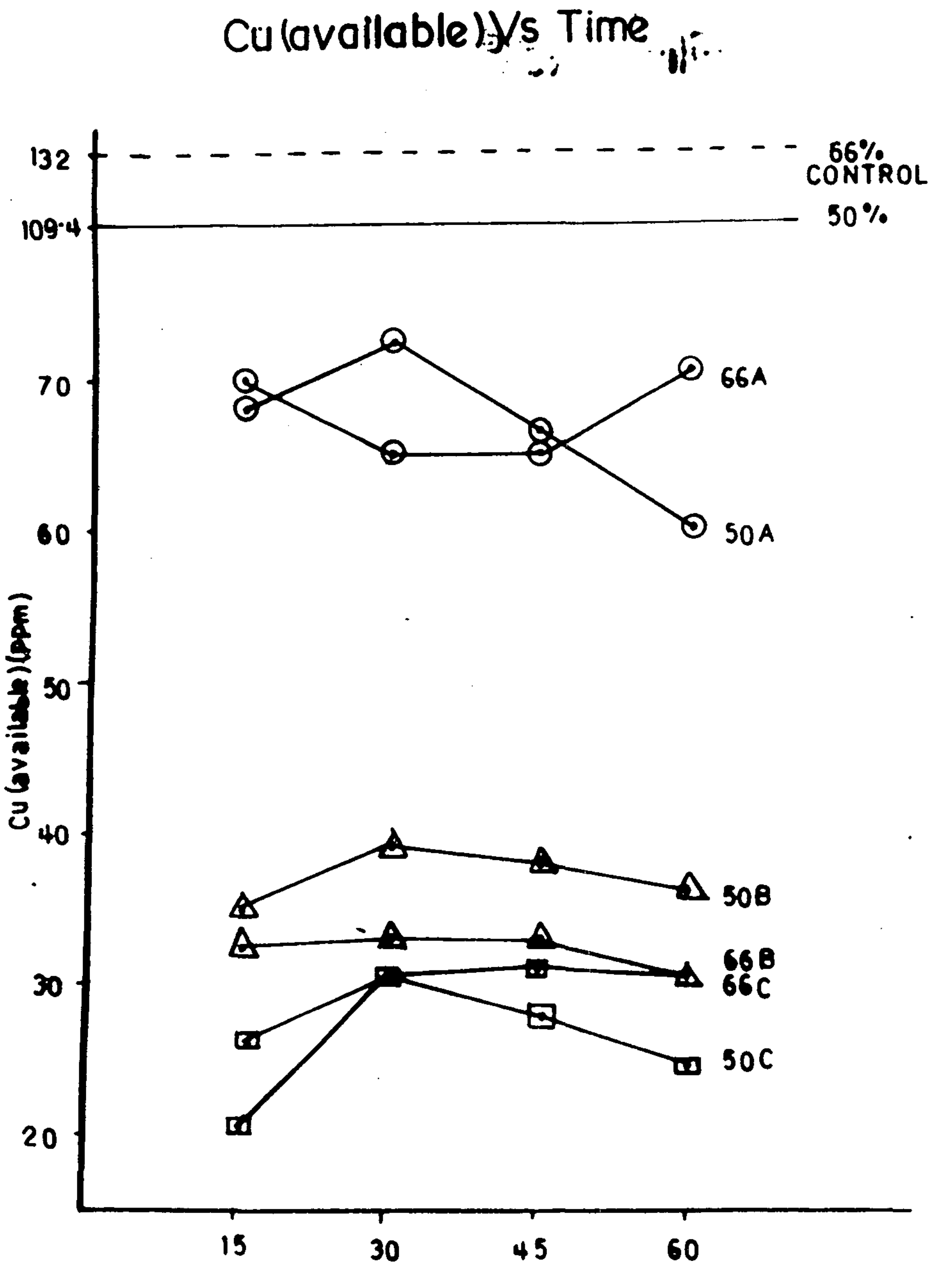


Fig.23. Periodic changes in Cu-Available (ppm) of 50% and 66% S-T mixtures due to liming.

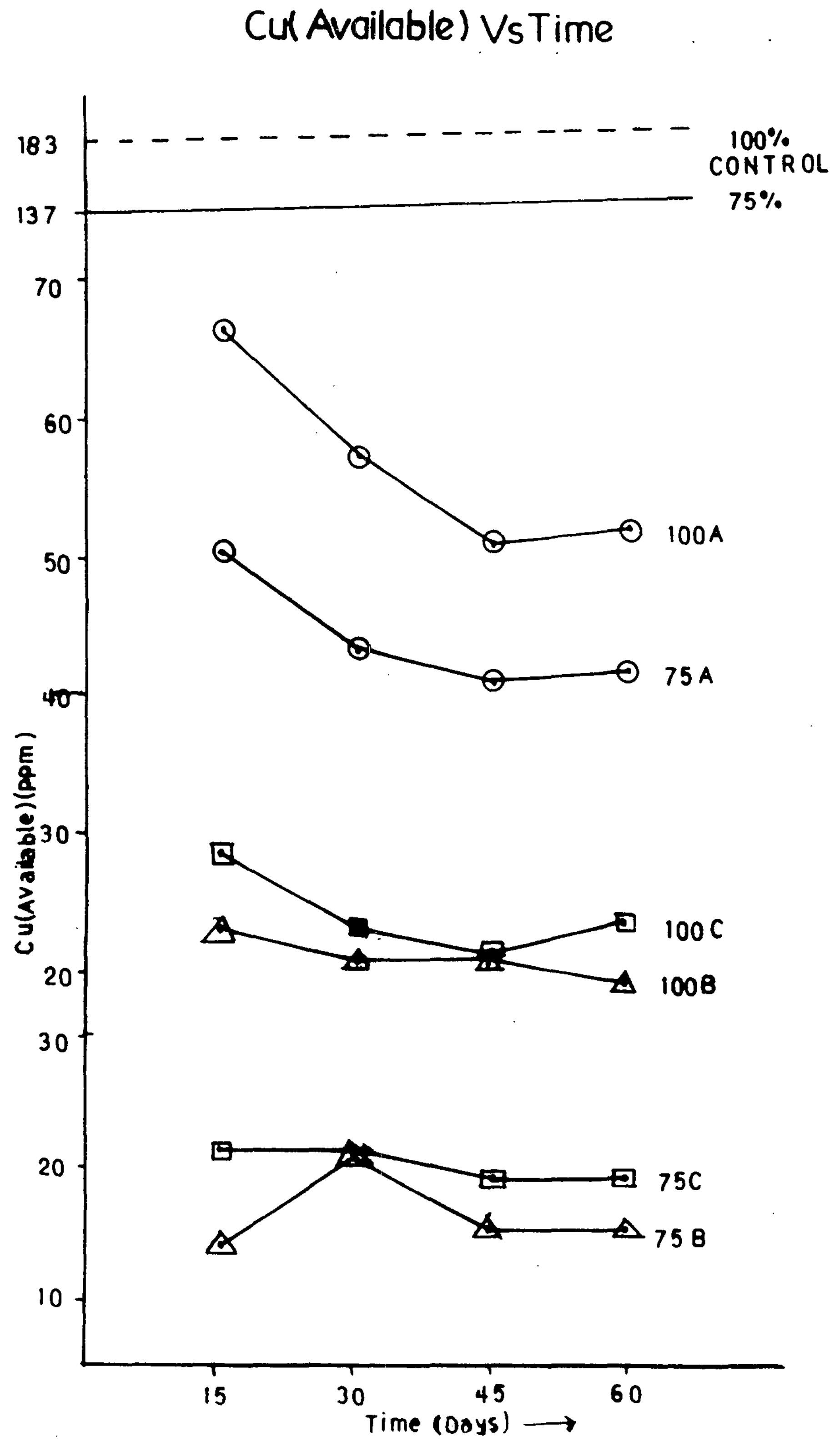


Fig.24. Periodic changes in Cu-Available (ppm) of 75% S-
mixtures and tailings due to liming.

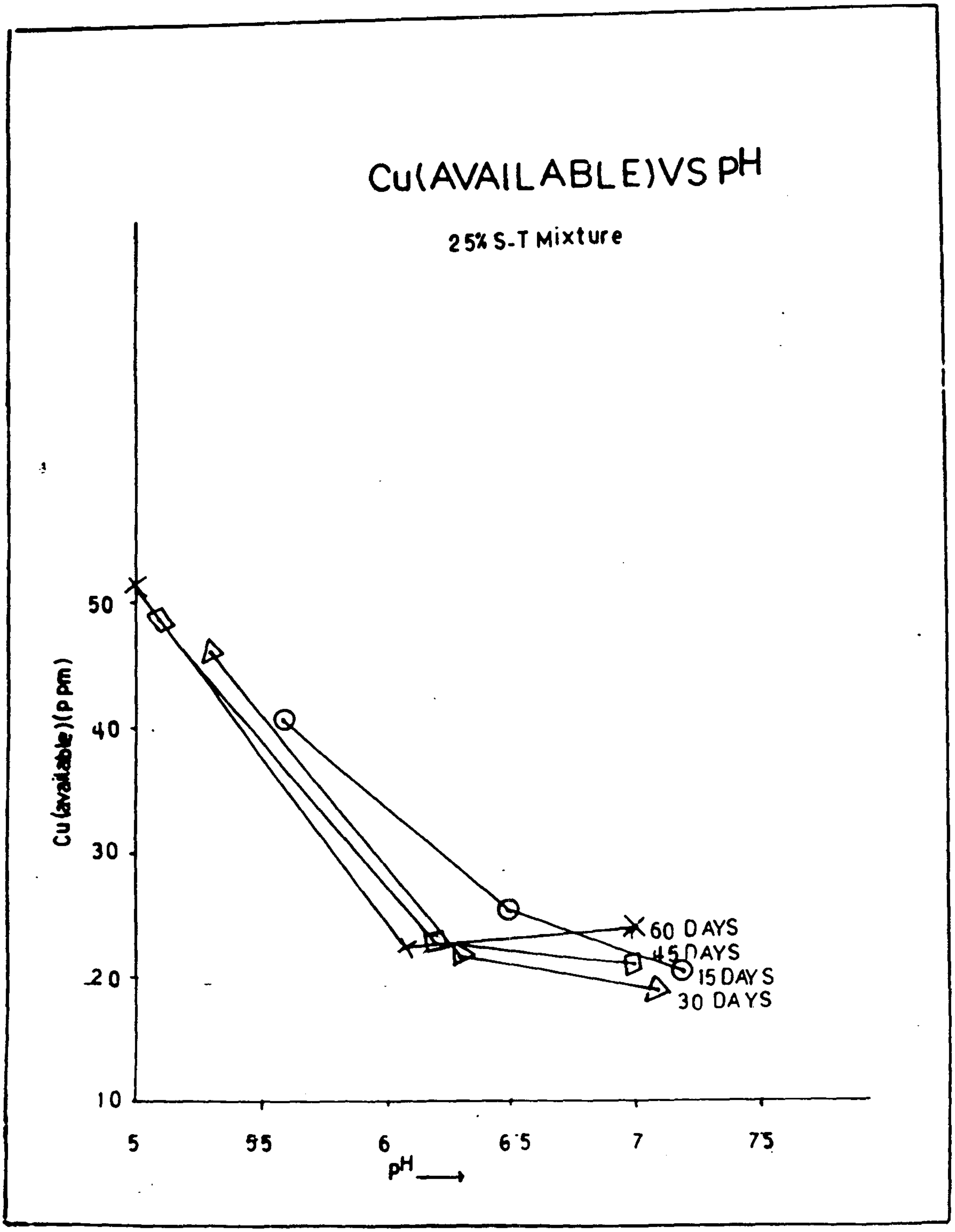


Fig.25. Effect of liming (pH) on Cu-Availability 25% S-T mixture over a period of 60 days.

may be the hydrolysis of Zn^{2+} ion into its hydroxide with the development of alkalinity in soil and soils like system after liming.

COPPER (AVAILABLE)

Periodic variations of available copper in different soil-tailings mixtures with different amount of lime additions are shown in Table - 13 and Fig. 21 to 23. Availability of copper in soil-tailings mixtures decreased following liming with all doses of lime additions and decrease was more in the case of lime addition equal to lime requirement and twice the lime requirement. In the high tailings percentage mixtures, however copper availability increased slightly for the lime requirement (C) than to the lime requirement (B) lime addition.

Periodic variations of copper availability increases from 15 days after liming for the mixtures high in soil percentage adn this periodic increase decreases as the percentage of tailings increases and finally it showed a decreasing trends for the lime additons equivalent to half of lime requirement. Other two lime additions did not show any uniform trend over time. However, the availabel copper was much less then the contol level after 60 days of liming in all the cases.

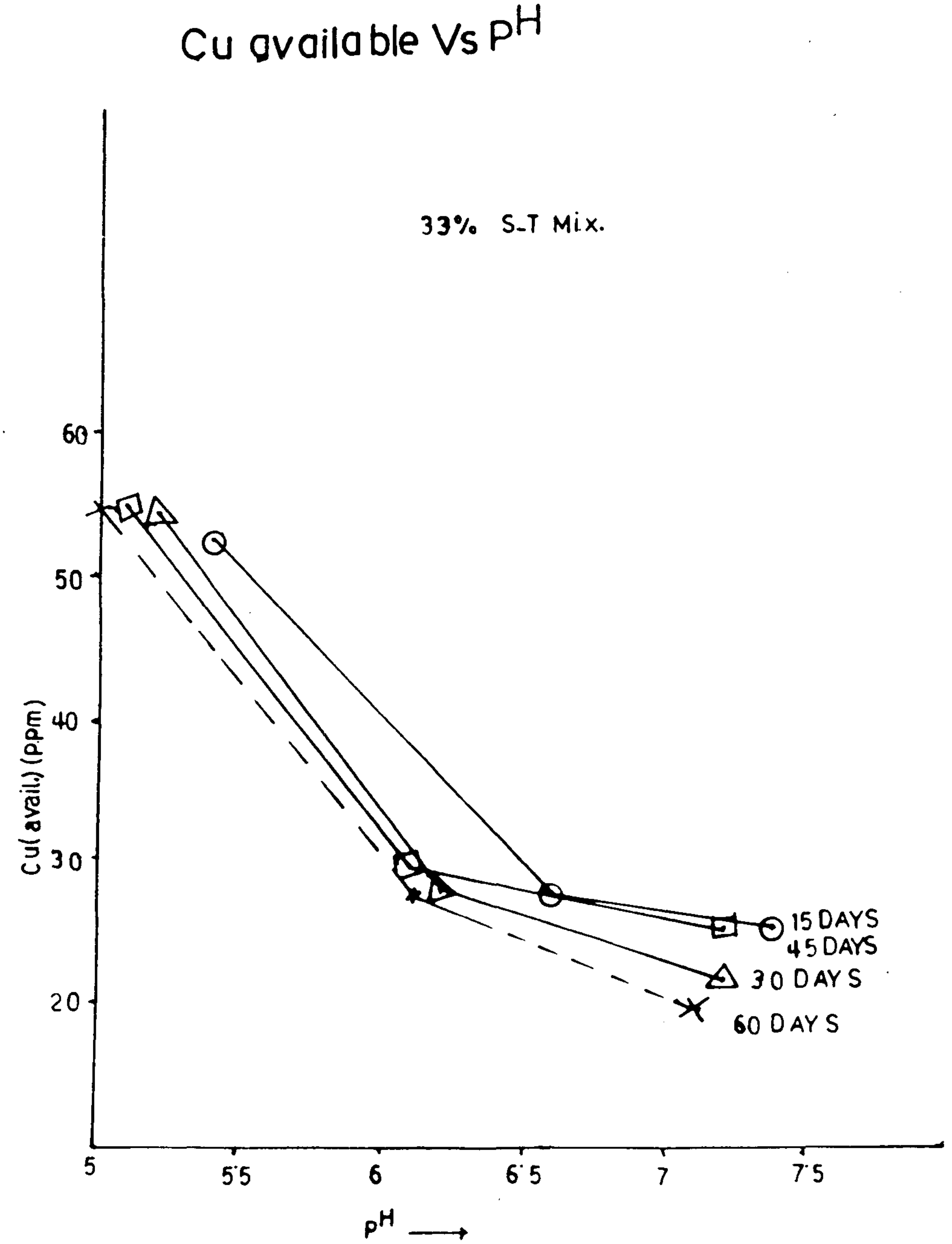


Fig.26. Effect of liming (pH) on Cu-Availability 33% S-T mixture and tailing over a period of 60 days.

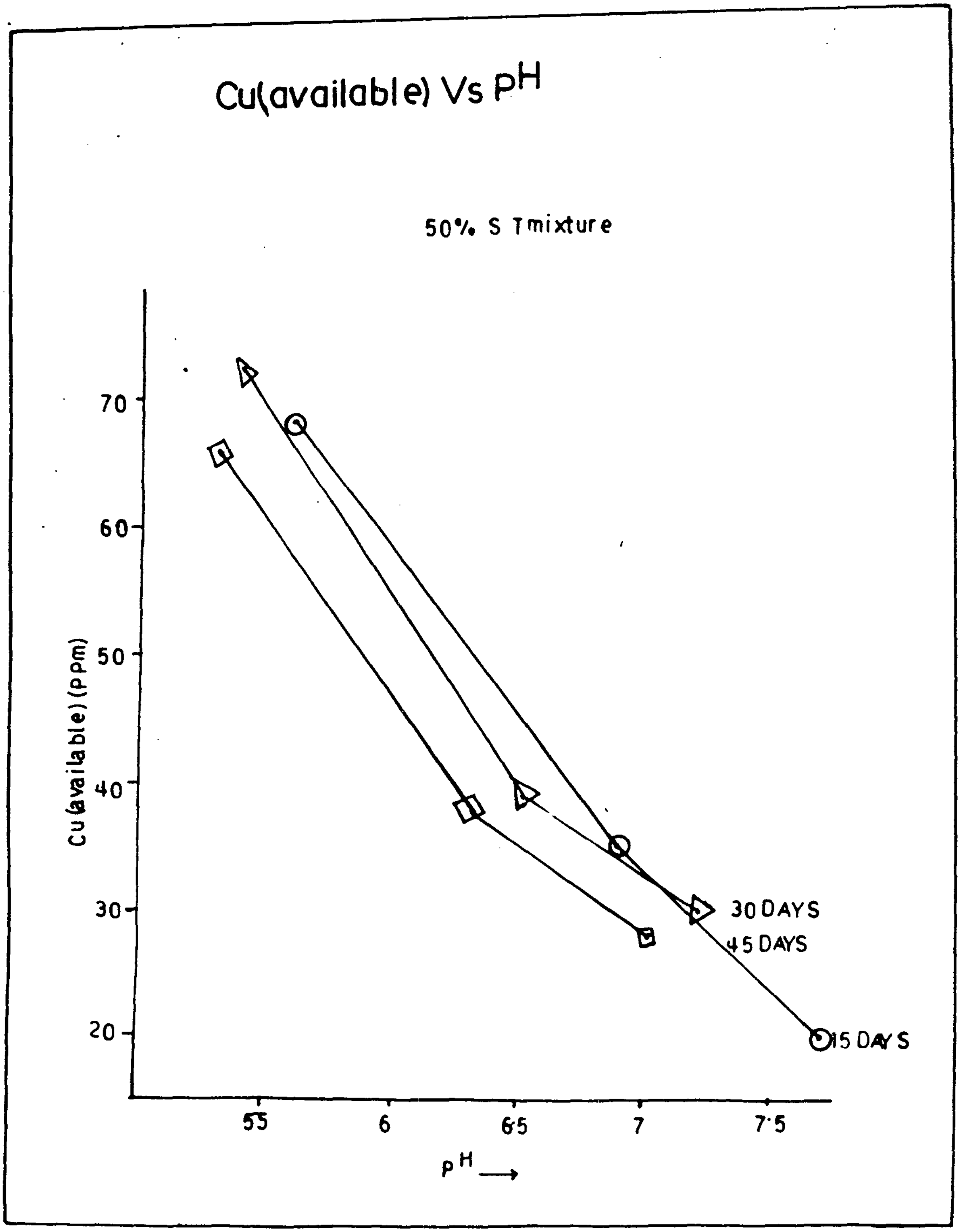


Fig.27. Effect of liming (pH) on Cu-Availability 50% S-T mixture over a period of 60 days.

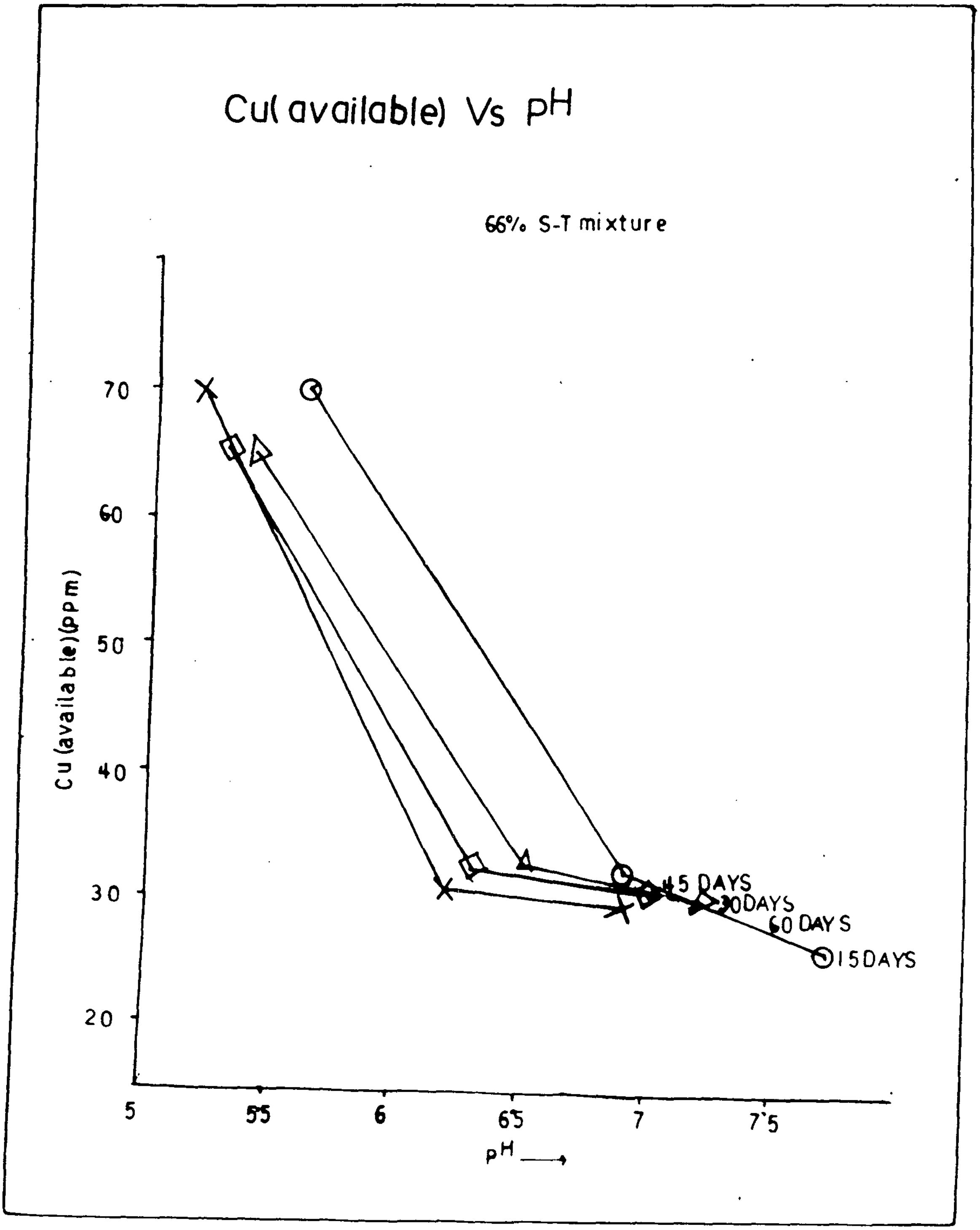


Fig.28. Effect of liming (pH) on Cu-Availability 66% S-T mixture and tailing over a period of 60 days.

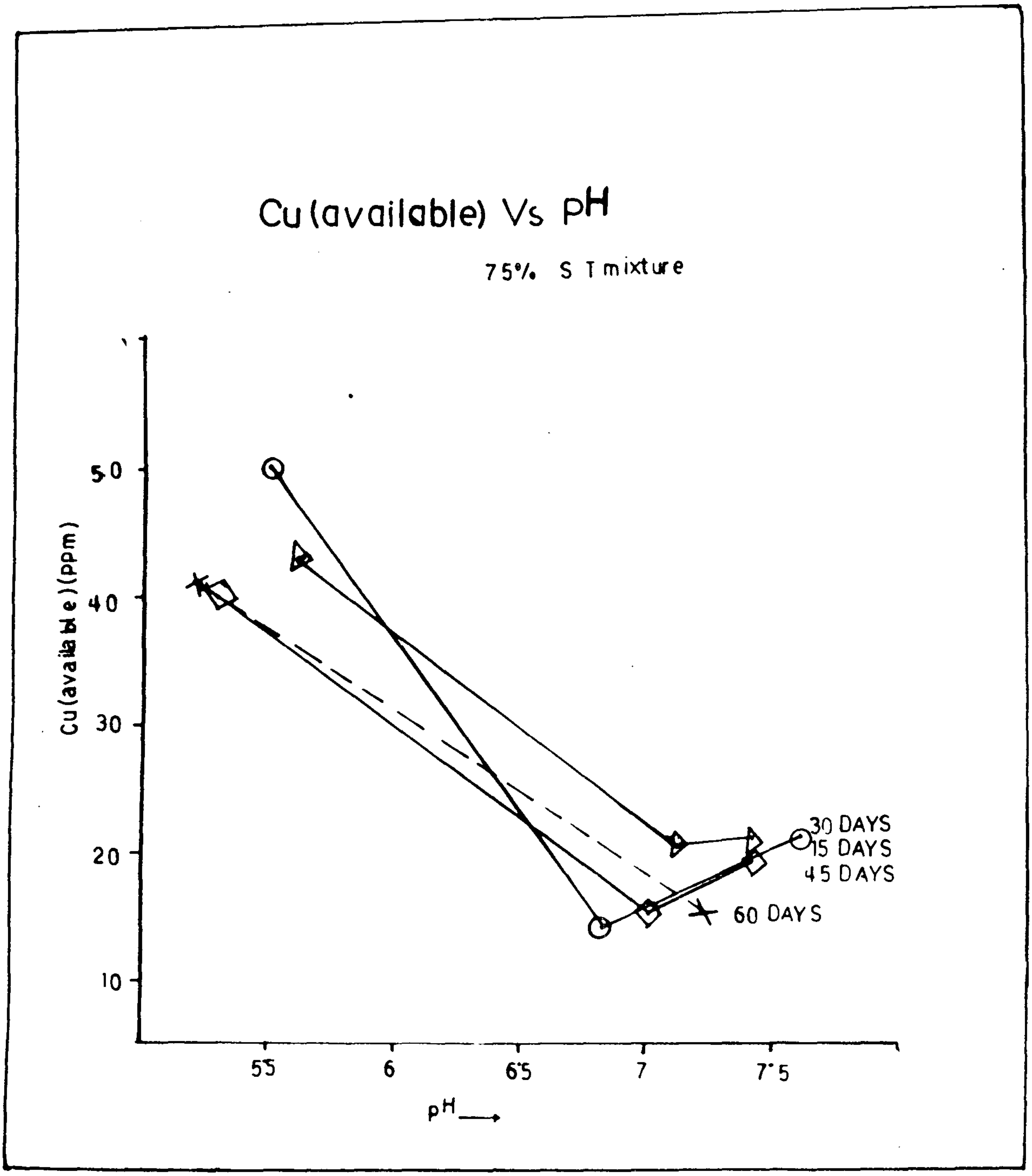


Fig.29. Effect of liming (pH) on Cu-Availability 75% S-T mixture over a period of 60 days.

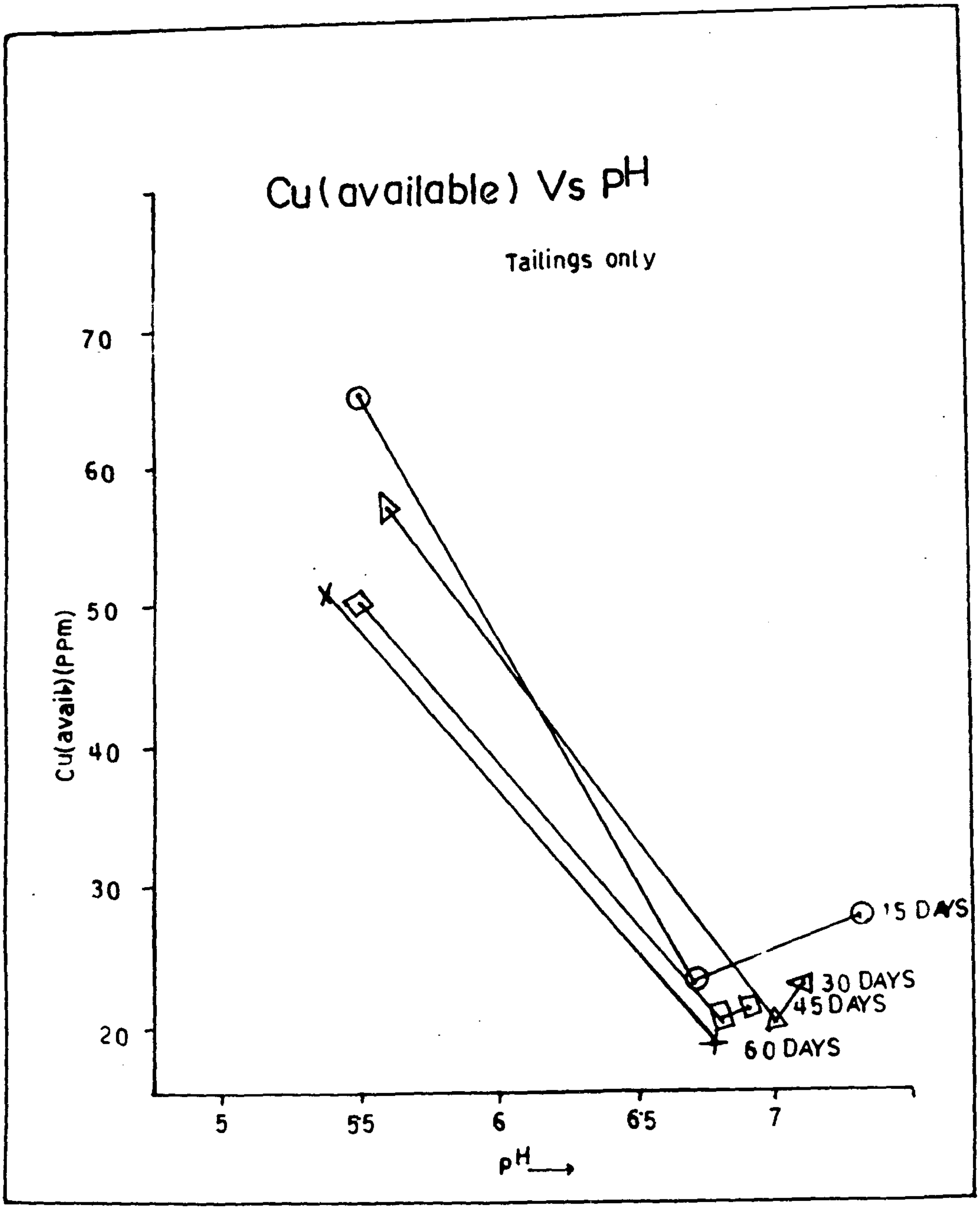


Fig.30. Effect of liming (pH) on Cu-Availability of tailing over a period of 60 days.

From the Fig. 24 to 29, it is evident that with increase in pH the availability of copper decreases for all the lime additions till 66% soil tailings mixture but in other two mixtures it increases after pH 7. So all the periodic variations of copper availability may be correlated with pH. In high soil percentage mixture the two were well correlated, whereas in high tailings percentage mixtures, not well correlated.

As the pH increases Cu^{2+} from solution is likely to precipitate as $Cu(OH)_2$, and decrease in copper availability with increasing pH is probably due to the preference of soil exchange sites for hydrolysis products of this metal. At high pH Cu is thus bound to silicate clays through ion exchange or fixation process and also by the promotion of surface hydrolysis (cavallaro and Mcbride, 1980).

So the periodic variations and the decrease in the copper availablity following liming may be accounted for the hydrolysis of Cu^{2+} and removal of Al^{3+} and H^+ from ehcanges sitees and adsorption ofCu on Fe and Al hydroxides (Kinniberg et. al., 1976)

The incease in copper availability in the case of 75% mixture and tailings above pH 7 may be attributed to solubilized organic complexing agents (Saeed and Fox, 1977.)

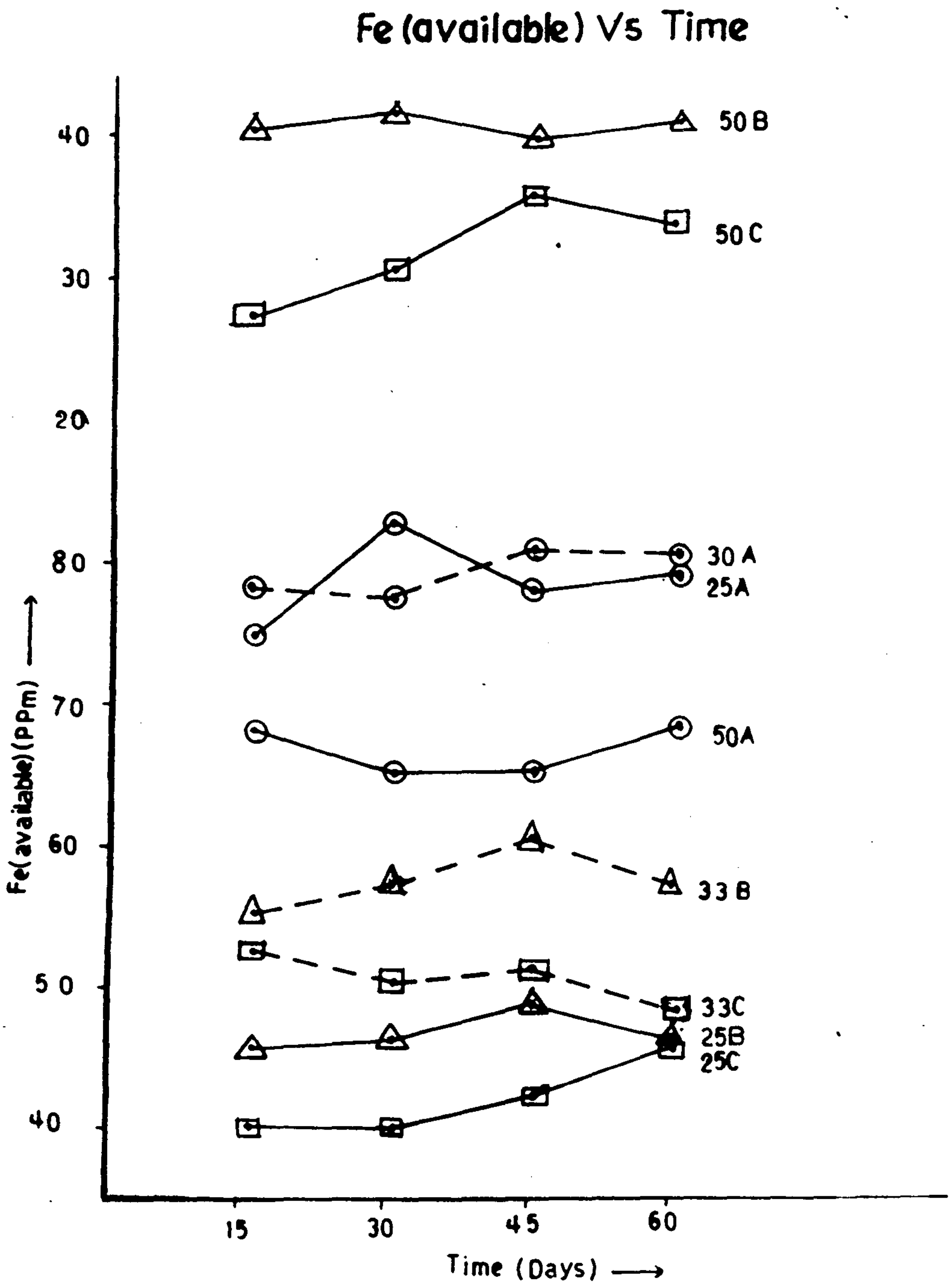


Fig.31. Periodic changes in Fe-Available (ppm) of 25% and 33% S-T mixtures due to liming.

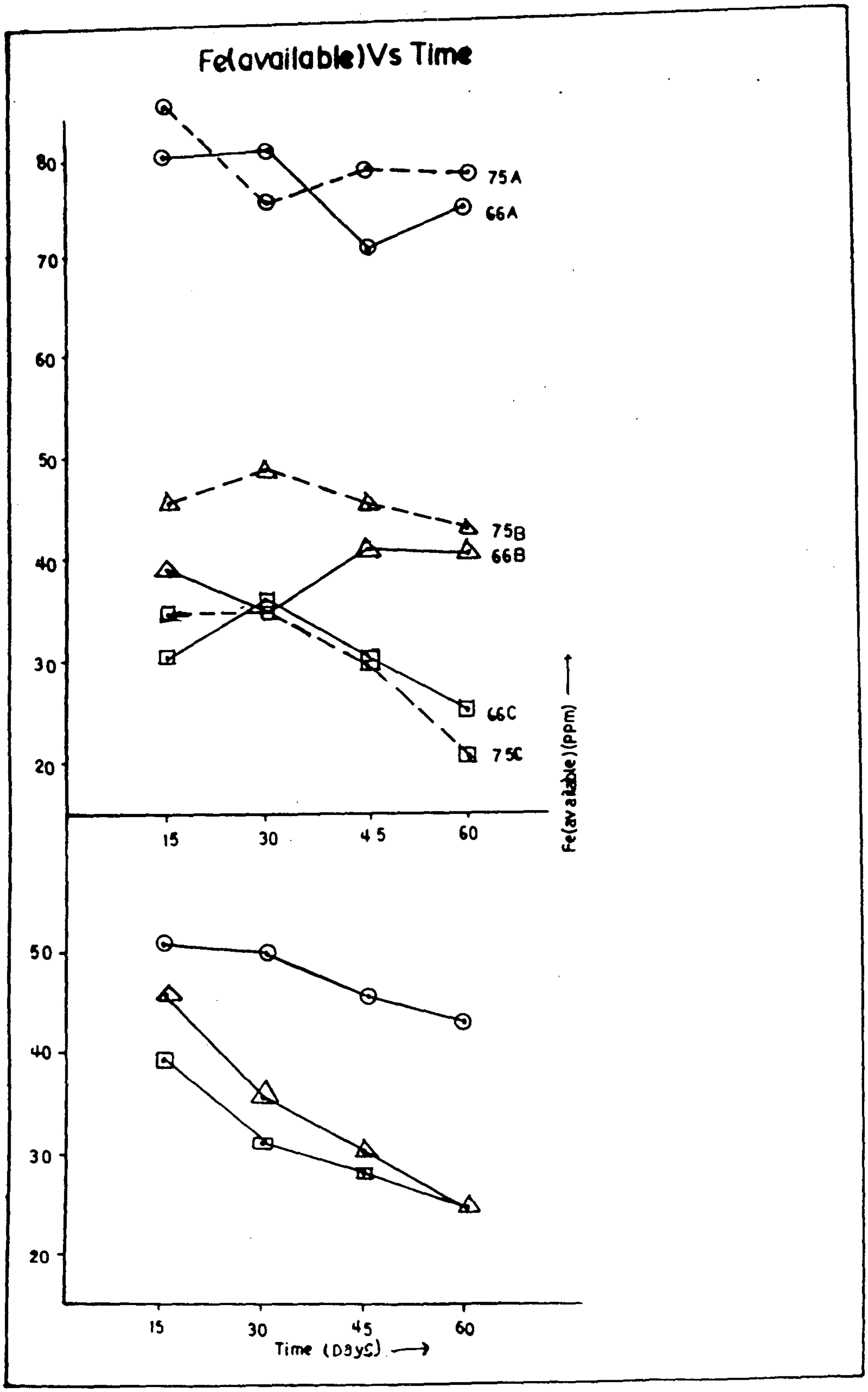


Fig.32. Periodic changes in Fe-Available (ppm) of 66% and 75% S-T mixtures due to liming.

IRON (AVAILABLE)

From the Table - 15 which gives periodic changes in available iron content of different soil-tailings mixture with different lime additions,it can be concluded that iron availability finally decreased by liming and the decrease in avaliable iron content was higher with higher amount of lime addition for a particular soil-tailings mixture and tailings itself. Periodic variations for the available iron showed decreasing or increasing trends for different soil-tailings mixtures with different amount of lime additions, but the availbale iron content 60 days after liming were found to be less to far less corresponding to low and high amount of lime added than available iron content of particular soil-tailings mixtures and tailings.

From the Fig. 30 & 31 and Table - 15, it can be observed that in mixtures high in soil percentage the available iron content showed decrease in its periodic value but found to increase peridically in high tailings percentage mixtures and tailings for half of lime requirement lime-addition. Amount of lime added equivalent to lime requirement have slight or no influence on the periodic changes of availability of iron, except in tailings where it decreased periodically. Decreasing periodic change

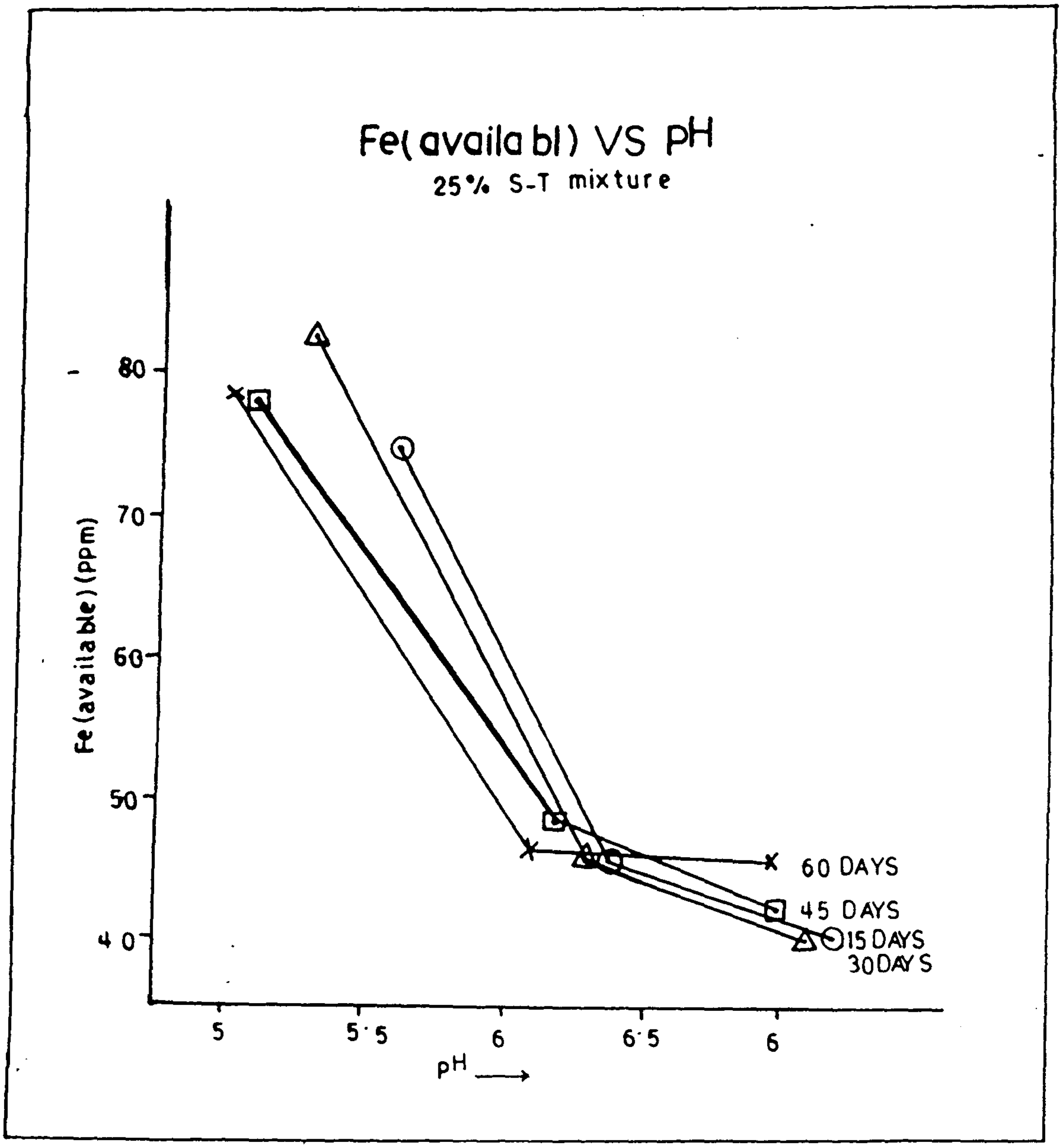


Fig.33. Effect of liming (pH) on Cu-Availability 25% S-T mixture over a period of 60 days.

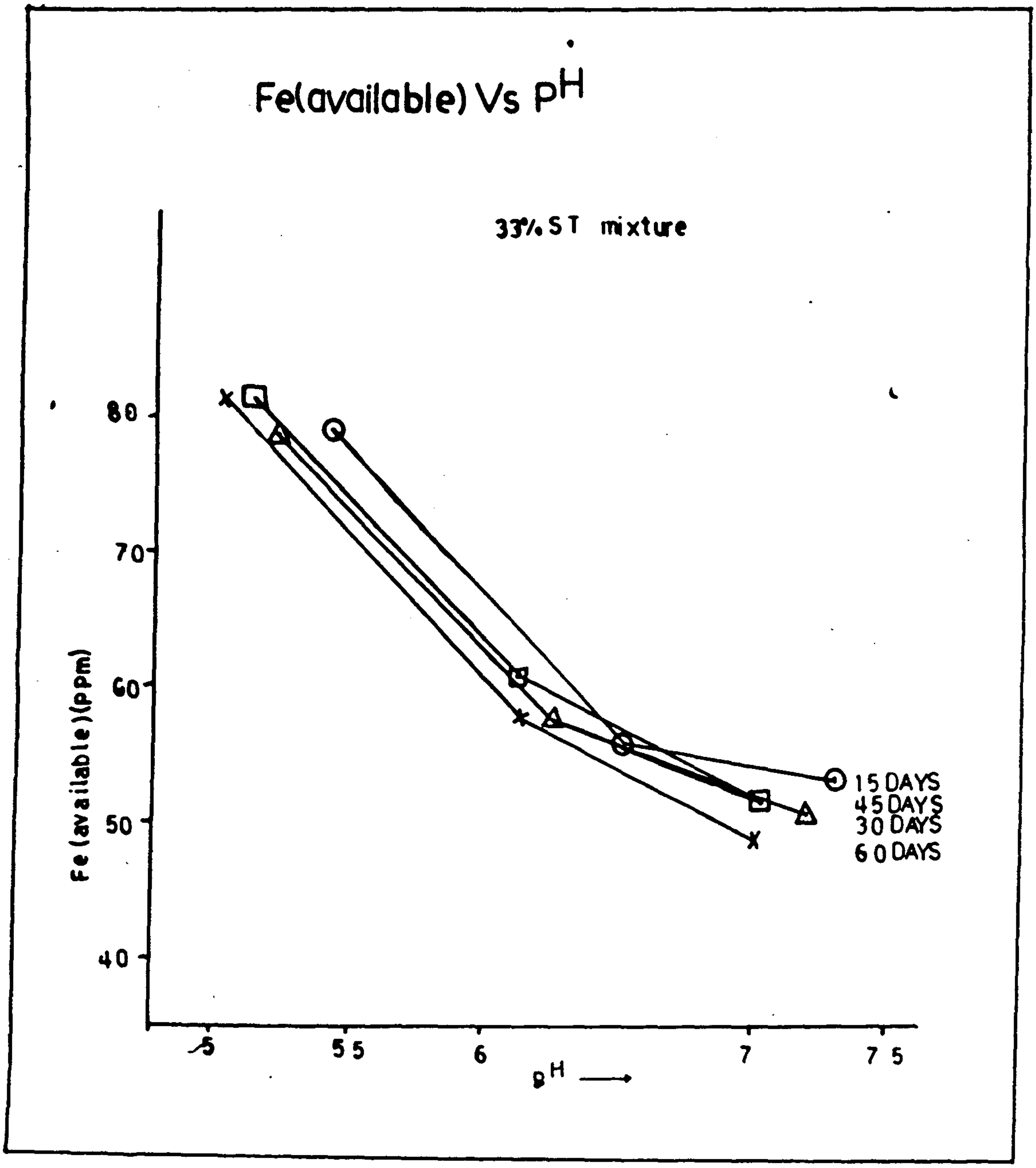


Fig.34. Effect of liming (pH) on Cu-Availability 33% S-T mixture over a period of 60 days.

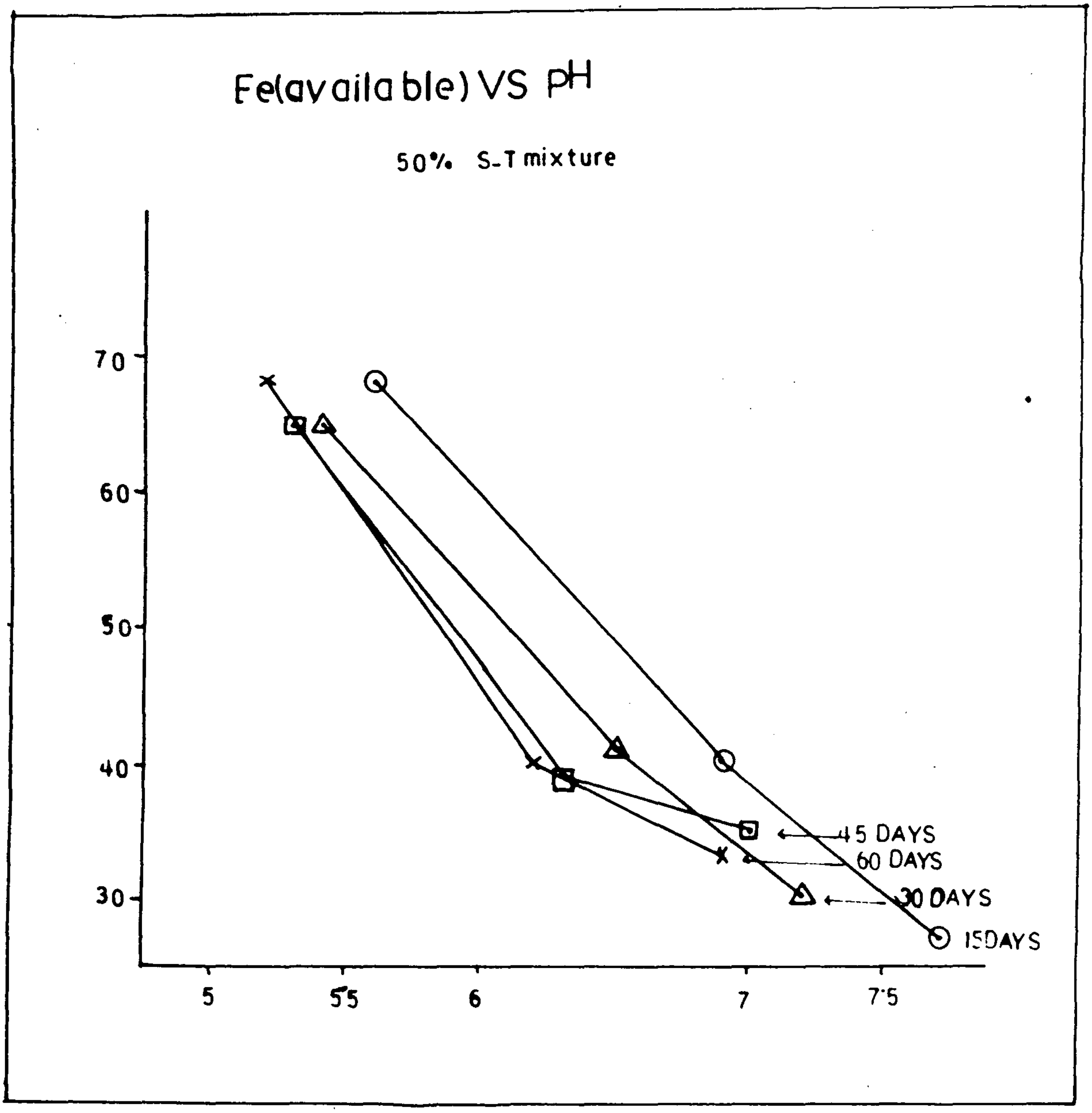


Fig.35. Effect of liming (pH) on Cu-Availability 50% S-T mixture over a period of 60 days.

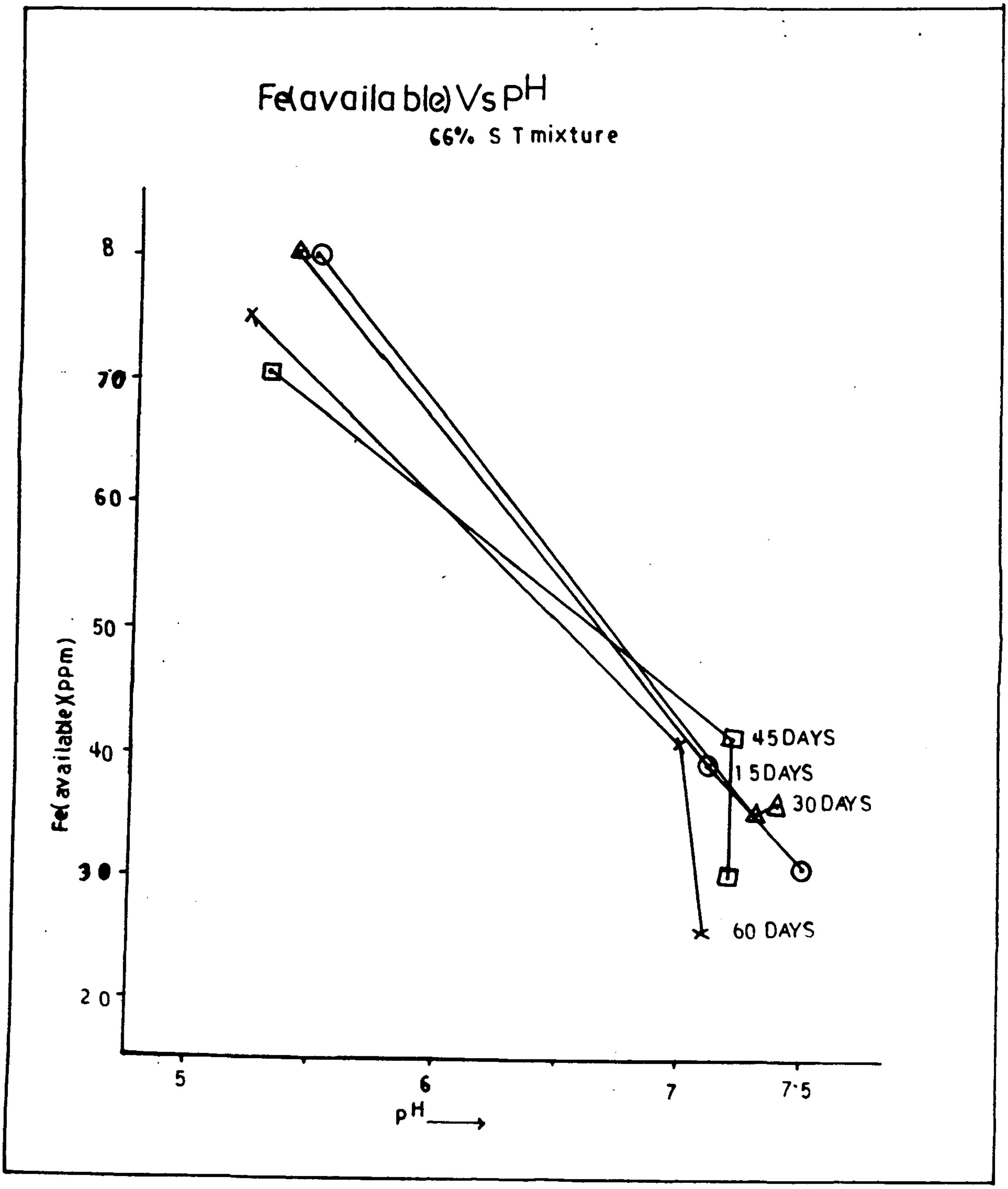


Fig.36. Effect of liming (pH) on Cu-Availability 66% S-T mixture over a period of 60 days.

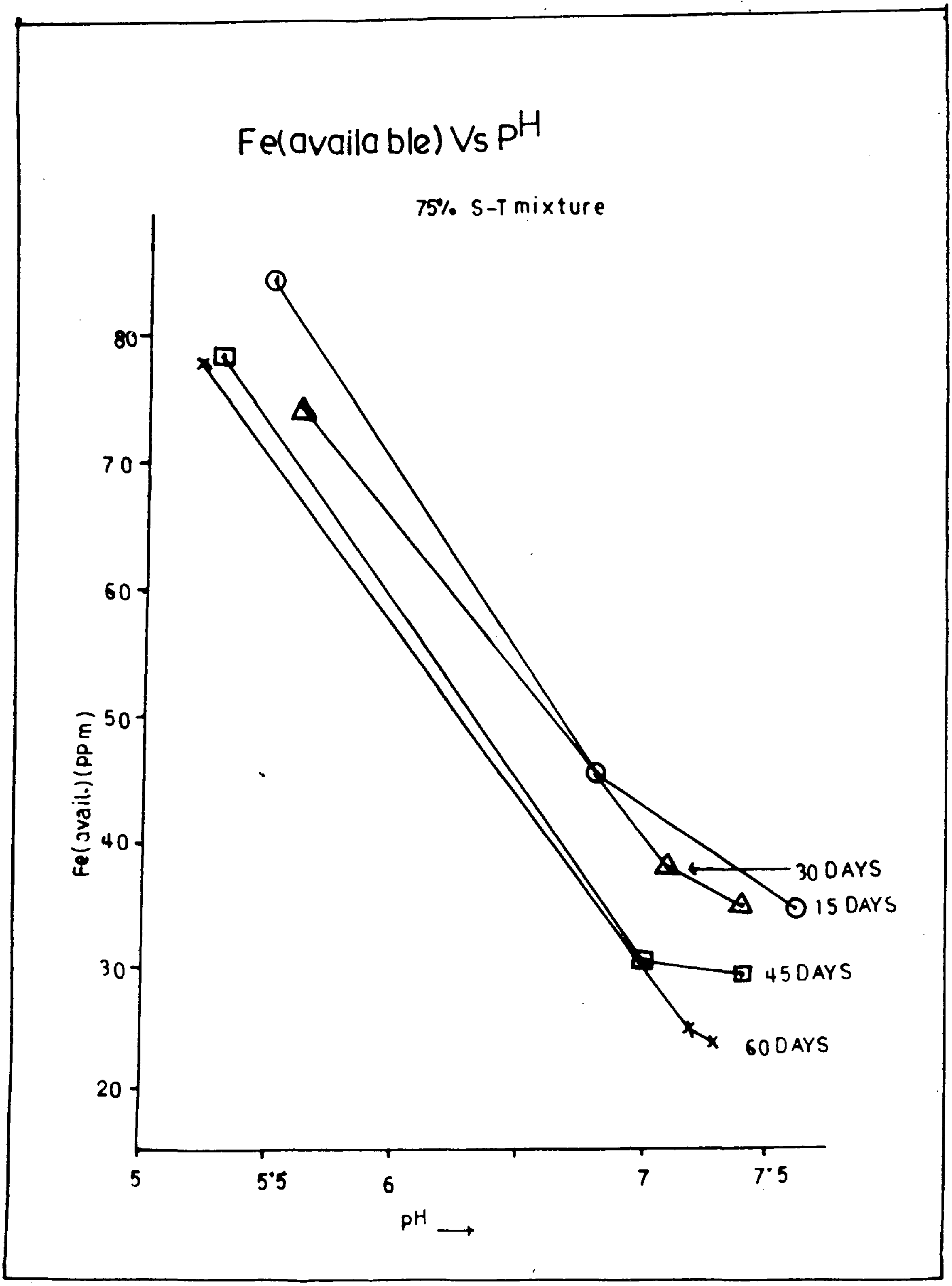


Fig.37. Effect of liming (pH) on Cu-Availability 75% S-T mixture over a period of 60 days.

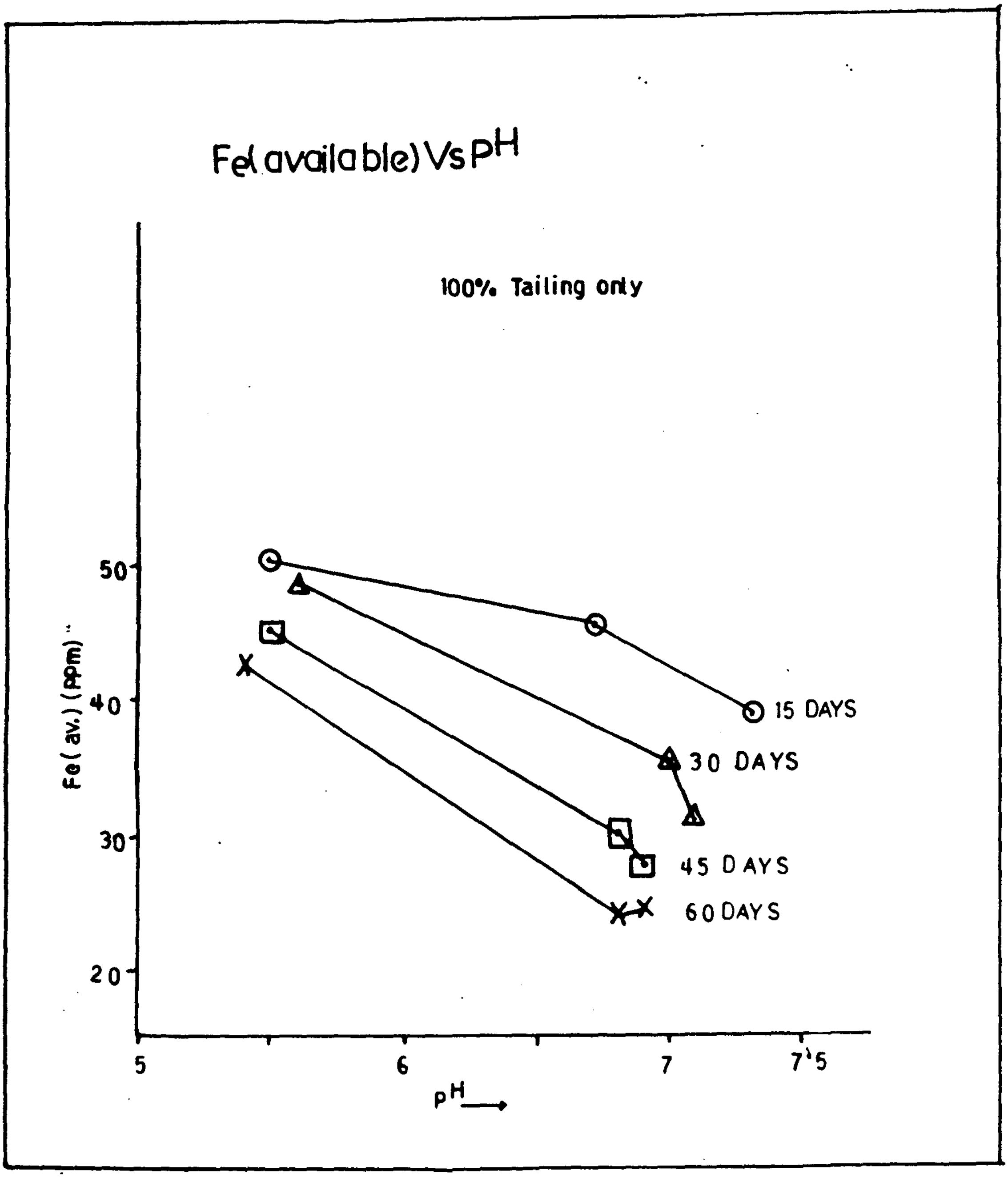


Fig.38. Effect of liming (pH) on Cu-Availability of tailings over a period of 60 days.

in most of the cases were found where twice the amount of lime was added.

We find that iron availability like kother heavy metals, also decreased with increasing pH of the system and we can say in general pH was most prominant factor that controlled the availability of iron.

The reduction in iron availability following liming may be apprently due to abundance of Ca++ ions due to lime addition (Datta and Gupta, 1984). The soil reaction, lime content etc. may influence available iron content by affecting the redox potential and hydration and dehydartion of iron compounds in soils and soils like system (Hoshiar singh, 1964). Another process which can govern the solubility is the solubility of iron compounds, specific surface reaction of iorn with soil colloidalconstituents. Thus the adsorption of hydrolysed species and iron itself and precipitation of metal hydroxides in alkaline media may be proposed as mechanism likely to control the solubility of iron in soils and soil like materials.

CORRELATION BETWEEN pH AND OTHER PARAMETERS

Among available nitrogen, phosphorous and pottasium, nitrogen and phosphorous were very highly positively correlated with pH for different soil-tailings mixtures and tailings. Correlation coefficients of available nitrogen with pH were found to varry from r=o.8153 to r=0.9173 (Table 16 to 21). This means that the variations in nitrogen due to variations in pH was in the range of approximately 64% to 81% for different soil tailings mixtures and tailings. Available phosphosrous was even more highly correlated with pH than available nitrogen (Table - 16)

Available potassium showed well negative correltation with pH for 25% to 66% soil-tailings mixtures, but there was no correlation for 75% mixture and insignificant negative correlation for tailings (Table - 18).

All the three heavy metals under study were highly negatively correlated with pH, with few exceptions in correlation of available copper with pH (r=-0.2137 and r=-0.2228) (Table - 19)

SUMMARY AND CONCLUSION

SUMMARY AND CONCLUSION

The study conducted on the effect of lime on the changes of physico-chemical properties of tailings amended soils from Khetri area, gives a general view of amelioration of soil acidity problem. The study was planned to asses the suitability of application of lime requirements vis-a-vis improvement of soil fertility status of the ameneded mine disturbed land within the span of 60 days.

Experimental results revealed that liming at various doses to different soil-tailings mixtures produced better results in terms of availability of nitrogen, phosphorous and reduction in toxicity of heavy metals, but decreased the availability of potassium.

Soil ammended with the high tailings rate and pure tailings resulted into unfavourable soil perameters for proper plant growth due to low level of major nutrients.

Begining with a soil-tailings mixture with a lower percentage of tailings and moving towards a higher percentage of tailings in the mixtures, a corresponding change in the periodic variation of a particular parameter has been observed.Few cases reflect a reversal of trend, while in few other cases, a deteriorating pattern was observed. Lime application resulted in lowering the total N % of the soil tailings mixtures and tailings, while in the case of total P and K, they maintained more or less constant values during the total period of the experiment.

The findings of the present investigation suggest that liming at proper dose with optimum moisture is effective in not only rectifying but also improving the quality of degraded lands due to copper tailngs generated from surface mining and ore processing at Khetri.However, further studies are needed regarding the variability of parameters like temperature, moisture content, lime quality to have better understanding of the problem. While the observations demonstrated definite positive influence of the lime application on the availability of nitrogen and phosphorous, its effect on potassium availability was in the negative direction which required further details investigation. Liming, necessarly produced better results, but it is not to a level where plants can grow properly. Although liming reduced the concentrations of various heavy metals largely, but still the metal concentrations in tailings amended soil remained in the toxic range. Therefore, a mechanism has to be developed to reduce the concentration of heavy metals further. Moreover, few other amendments such as sewage sludge, flyash, pressmud etc. could be tried in different proportion either individually or collectively to asses their suitability in utilization of copper tailings for land applications. A long term field experiments in this regard based on appropritate statistical design will be needed to evolve any suitable technology for disposal of copper tailings on land applications.

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